

# THE NITROGEN SYSTEM OF COMPOUNDS

BY

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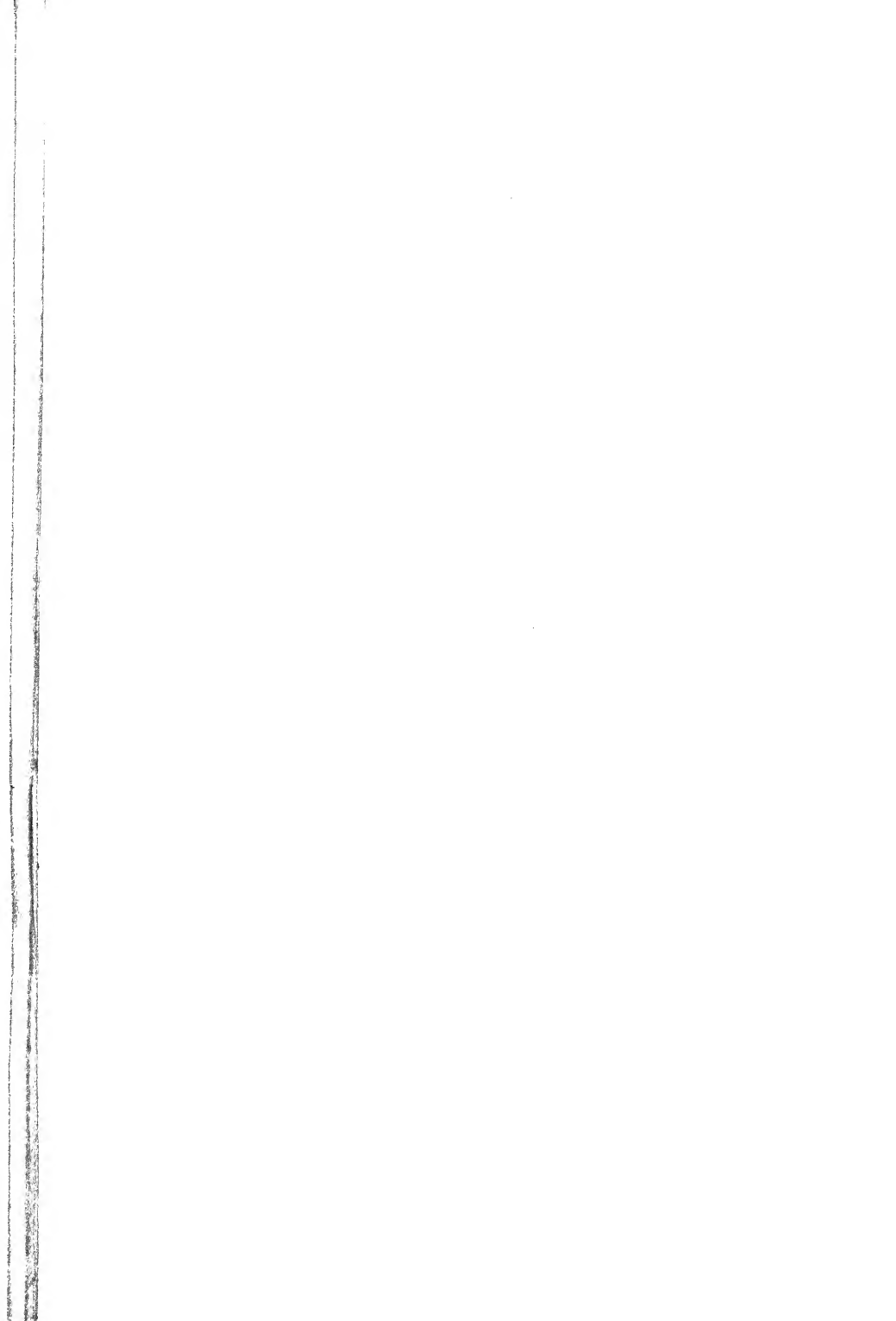
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## GENERAL INTRODUCTION

### American Chemical Society Series of Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in cooperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, Secretary of the American Chemical Society, Washington, D. C.; John E. Teeple, Treasurer of the American Chemical Society, New York City; and Professor Gellert Allen of Swarthmore College. The Trustees have arranged for the publication of the American Chemical Society series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company (Reinhold Publishing Corporation, successors) of New York City.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed the editors, named at the close of this introduction, to have charge of securing authors, and of considering critically the manuscripts prepared. The editors of each series will endeavor to select topics which are of current interest and authors who are recognized as authorities in their respective fields. The list of monographs thus far secured appears in the publisher's own announcement elsewhere in this volume.

The development of knowledge in all branches of science, and especially in chemistry, has been so rapid during the last fifty years and the fields covered by this development have been so varied that

it is difficult for any individual to keep in touch with the progress in branches of science outside his own specialty. In spite of the facilities for the examination of the literature given by Chemical Abstracts and such compendia as Beilstein's *Handbuch der Organischen Chemie*, Richter's *Lexikon*, Ostwald's *Lehrbuch der Allgemeinen Chemie*, Abegg's and Gmelin-Kraut's *Handbuch der Anorganischen Chemie* and the English and French Dictionaries of Chemistry, it often takes a great deal of time to coordinate the knowledge available upon a single topic. Consequently when men who have spent years in the study of important subjects are willing to coordinate their knowledge and present it in concise, readable form, they perform a service of the highest value to their fellow chemists.

It was with a clear recognition of the usefulness of reviews of this character that a Committee of the American Chemical Society recommended the publication of the two series of monographs under the auspices of the Society.

Two rather distinct purposes are to be served by these monographs. The first purpose, whose fulfilment will probably render to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a readable form, intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs will enable such men to form closer contact with the work of chemists in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well-digested survey of the progress already made in that field and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, it is intended to include extended references to the literature, which will enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection will be made of those papers which are most important.

The publication of these books marks a distinct departure in the policy of the American Chemical Society inasmuch as it is a serious

attempt to found an American chemical literature without primary regard to commercial considerations. The success of the venture will depend in large part upon the measure of cooperation which can be secured in the preparation of books dealing adequately with topics of general interest; it is earnestly hoped, therefore, that every member of the various organizations in the chemical and allied industries will recognize the importance of the enterprise and take sufficient interest to justify it.

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## INTRODUCTION

Excepting fluorine, oxygen is the most powerfully negative of the elements. In view of this situation it becomes reasonable to ascribe to oxygen a dominating rôle, so to speak, in all its compounds, excepting its fluoride, and to regard all the metallic oxides and non-metallic oxides, the oxygen acids, bases and salts, the alcohols, aldehydes and other compounds containing oxygen as constituting an oxygen system of compounds. Just as reasonably one may look upon all oxygen compounds, excepting again oxygen fluoride, as derivatives of water and say that they belong to a water system.

Next to oxygen in the order of negativity stands nitrogen.<sup>1</sup> Such being the case it is reasonable to say that the compounds of nitrogen, excepting the fluoride and oxides which belong respectively to the fluorine system and the oxygen system, constitute a nitrogen system of compounds in the same sense that the compounds of oxygen have been assumed to make up an oxygen system. Nitrogen, with its high negativity, may be said to dominate all the compounds into which it enters excepting those with fluorine and oxygen. That is to say, all nitrogen compounds, with the exceptions noted, may be regarded as derivatives of ammonia and as such said to constitute an ammonia system. Since, however, it is the nitrogen contained in these compounds, rather than the ammonia from which they may be assumed to be derived, which gives them such properties as they have in common it seems better to speak of a nitrogen system of compounds rather than of an ammonia system, though of course it is a matter of no fundamental importance which designation is used.

In order to give credit to a man for what may properly be regarded as a brilliant idea the following bit of history is interjected here. In the autumn of 1896 Hamilton P. Cady, then an undergraduate, and now Professor of Chemistry at the University of Kansas, was working at the regulation course in quantitative analysis. Observing after a time that the young man was becoming bored with his task, the writer, at the time giving instruction in analytical chemistry, proposed to him that he prepare several of the cobalt-amine salts and confirm the composition of one or two of them by analysis. Some days later with a beautifully crystallized specimen

<sup>1</sup> Nitrogen is apparently somewhat more negative than chlorine. Pauling, *J. Am. Chem. Soc.*, **54**, 357 (1932).



of one of these interesting salts in his hand Cady stated that the ammonia in these and other salts containing ammonia must function in a manner very similar to that of water in salts with water of crystallization.<sup>2</sup> He suggested furthermore that liquid ammonia would probably be found to resemble water in its physical and chemical properties. As a direct consequence of Cady's suggestion has followed all the work done in this country on liquid ammonia.

As is familiarly known water occupies an outstanding position among solvents. In its capacity as a solvent for salts and as an ionizing agent it stands in a class by itself and is approached only by liquid ammonia and probably by hydrogen fluoride. Its heat of evaporation and its dielectric constant are the highest of any known substance, excepting that the dielectric constants of hydrogen peroxide and hydrocyanic acid are greater than that of water. Its specific heat and its critical constants are conspicuously high, while its ebullioscopic and cryoscopic constants are exceptionally low. It is an associated liquid, and it possesses in a high degree the property of forming compounds with salts and other compounds, the compounds with the former being known as salts with water of crystallization. All these properties tend to remove water far from other solvents and place it in a class by itself.

Of all known liquids ammonia most closely approaches water in all those properties which give to water its outstanding place among solvents. In its capacity as a solvent for salts liquid ammonia is secondary to water, though some salts, for example the iodides of mercury, lead and silver, which are insoluble in water, dissolve abundantly in liquid ammonia. It approaches water in its power of ionizing electrolytes. Solutions of salts in liquid ammonia are excellent conductors of electricity. It unites with salts as ammonia of crystallization, even surpassing water in its capacity for forming solvates. Like water it is an associated liquid. Its heat of vaporization is higher than that of any other liquid with the exception of water and hydrogen fluoride. For a substance of such simple composition its critical temperature and its critical pressure and even its boiling point at atmospheric pressure are remarkably high. Its specific heat is slightly greater than that of water while its ebullioscopic and cryoscopic constants are the lowest of any known solvent.

These striking resemblances between liquid ammonia and water lead one to expect to find the derivatives of ammonia following more or less closely in their properties and reactions those of the analo-

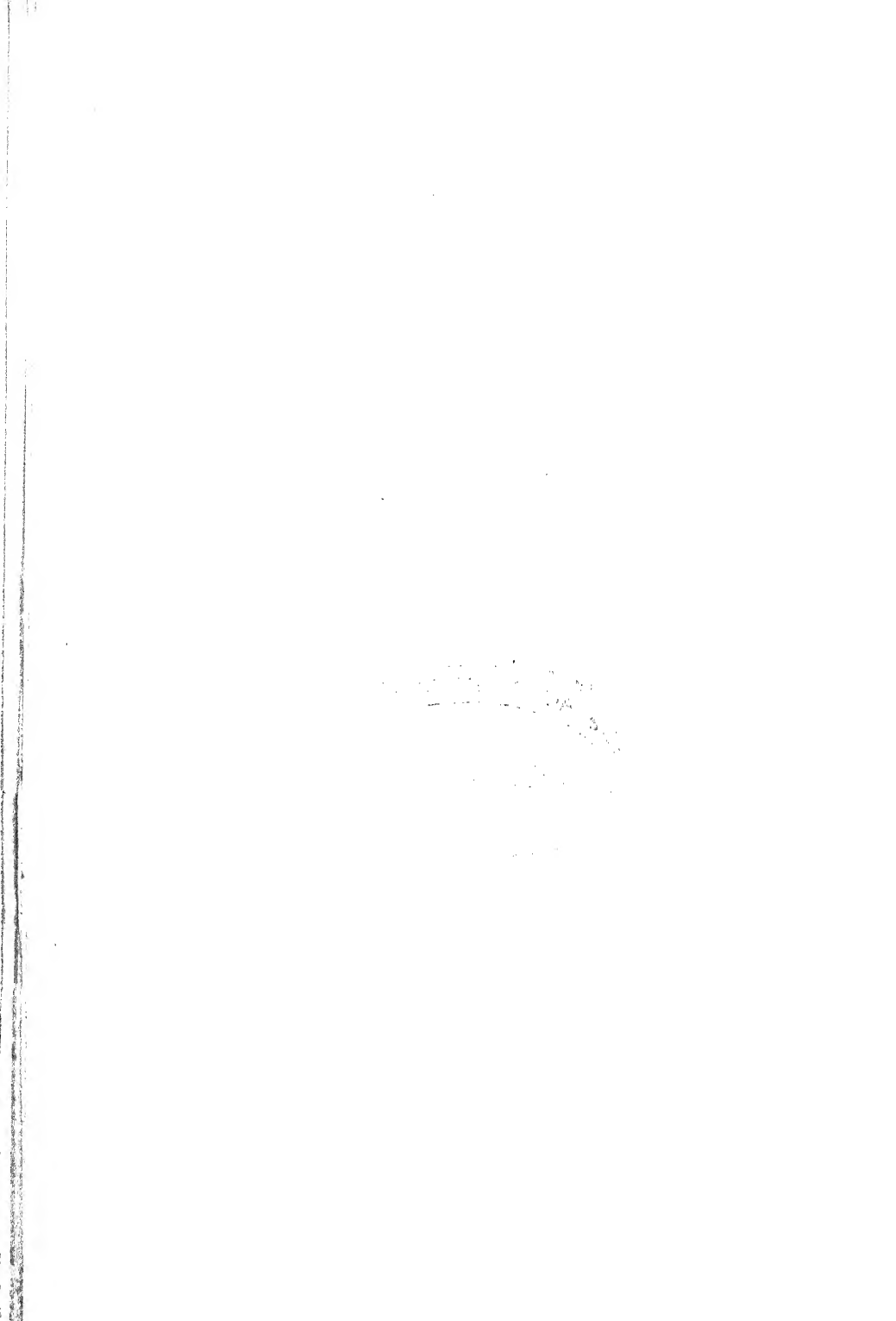
<sup>2</sup> The parallelism between water of crystallization and ammonia of crystallization was noted many years ago by Robert Kane and by Rose [*Ann. Chim. Phys.*, 72, 342, 346 (1839); Remsen, "Inorganic Chemistry," 2d. Ed., 593 (1890)].

gous water compounds or, stated in another way, the compounds of oxygen and nitrogen should be expected to show many properties in common. As a matter of fact the resemblances between the analogous derivatives of nitrogen and oxygen are hardly less striking than those enumerated above in comparing the properties of ammonia and water.

For example, potassium amide, which is a derivative of ammonia in the same sense that potassium hydroxide is a derivative of water, shows all the properties of a base. Acetamidine, as the nitrogen analog of acetic acid, meets our expectations in its behavior as an acetic acid. Acetamide shows the properties of a mixed acetic acid derived simultaneously from water and ammonia. Calcium cyanamide and calcium cyanate are just as certainly calcium carbonates as is the familiar limestone. The first salt belongs to the nitrogen system, the second is derived at the same time from ammonia and water, the third belongs to the oxygen system. Acids, bases and salts, alcohols, aldehydes and representatives of other classes of compounds containing nitrogen as their dominating element exhibit all the familiar properties of their analogous oxygen compounds.

The object of this monograph is to outline what we have chosen to call the nitrogen system of compounds and to bring to the attention of chemists the remarkable extent to which the compounds of nitrogen simulate in their properties and behavior the analogous compounds of oxygen.

Other systems of bases, acids and salts have been suggested, among them systems in which methane, hydrogen sulfide, and hydrogen fluoride, phosgene and hydrazine respectively are supposed to function as parent substances just as water and ammonia are assumed to do in the oxygen and nitrogen systems outlined above. The ideas underlying these suggestions are reasonable enough excepting that hydrazine and its derivatives are rather to be regarded as belonging to the nitrogen system just as hydrogen peroxide and its derivatives must be thought of as being members of the oxygen system while phosgene, in view of the outstandingly dominating character of oxygen, belongs to the oxygen system. Of course in case anything is gained thereby phosgene may be said to belong at the same time to the oxygen system and the hydrogen chloride system.



# CONTENTS

	PAGE
INTRODUCTION .....	9
CHAPTER I. PROPERTIES OF LIQUID AMMONIA .....	15
II. REACTIONS IN LIQUID AMMONIA .....	24
III. THE NITROGEN SYSTEM OF BASES, ACIDS AND SALTS..	30
IV. NOMENCLATURE .....	35
V. AUGMENTATION AND REDUCTION IN LIQUID AMMONIA	47
VI. AMMONO BASES AND BASIC NITRIDES.....	53
VII. ALKALI METAL SALTS OF AMPHOTERIC METALLIC AMIDES AND IMIDES .....	64
VIII. AMMONOBASIC SALTS .....	75
IX. MERCURY NITROGEN COMPOUNDS.....	80
X. AMMONO CARBONIC ACIDS .....	86
XI. AQUO-AMMONO CARBONIC ACIDS .....	108
XII. AMMONO CARBONOUS ACID .....	128
XIII. AMIDES AND IMIDES OF SILICON, TITANIUM, GERMA- NIUM, ZIRCONIUM, TIN AND THORIUM .....	135
XIV. HYDRAZOIC ACID .....	141
XV. AQUO-AMMONO NITRIC ACID .....	154
XVI. AMMONO AND AQUO-AMMONO PHOSPHORIC AND PHOS- PHOROUS ACIDS.....	160
XVII. AQUO-AMMONO SULFURIC ACIDS .....	167
XVIII. AMMONO SULFUROUS ACID, AMMONO-THIO SULFURIC ACID, AQUO-AMMONO SULFUROUS ACID AND SUL- FAYLIC ACID.....	172
XIX. AMMONO HYPOCHLOROUS ACIDS .....	177
XX. MIXED ACIDS .....	184
XXI. ACID ANAMMONIDES .....	188
XXII. ACID ANHYDRIDE-ANAMMONIDES .....	197
XXIII. ACID CHLORIDES .....	200
XXIV. HYDROGEN PEROXIDE, HYDRAZINE AND HYDROXYLAMINE	211
XXV. AMMONO ALCOHOLS .....	217

**Molecular Boiling Point Elevation.** The ebullioscopic constant of liquid ammonia, calculated by means of the equation,  $K = 0.0198T^2/\lambda$ , in which  $T$  represents the absolute boiling point of ammonia and  $\lambda$  its heat of vaporization, has the value 3.47.

In their early survey of the properties of liquid ammonia Franklin and Kraus<sup>1</sup> undertook the direct determination of this constant with the result that the molecular elevation of the boiling point of liquid ammonia was found to vary rather widely from solute to solute as well as with the concentration. Some of the experimental data are given in Table 2, in which the superscripts, g/100 G and K, represent respectively the concentrations in grams of solute per 100 grams of solvent and the observed molecular elevation of the boiling point.

TABLE 2.—Molecular Boiling Point Elevation.

g/100 G	K	g/100 G	K	g/100 G	K	g/100 G	K
Water		Ethyl Alcohol		Sucrose		Sodium Nitrate	
0.92	3.42	1.60	3.11	1.72	3.18	1.53	2.37
1.83	3.50	3.15	3.36	4.63	3.25	1.65	2.78
3.20	3.45	6.39	3.34	9.91	3.90	4.26	2.99
5.27	3.45	12.38	3.36	20.71	3.77	9.70	3.37
8.54	3.44	26.74	3.38	38.71	3.93	16.69	3.72
19.7	3.53	44.8	3.29	75.8	4.70	33.11	4.58
...	...	...	...	...	...	41.3	5.24

Water, as perhaps might have been expected, gave the most consistent results. One series of eleven measurements in which the concentration in respect to water ranged from 0.92 gram to 19.7 gram per 100 grams ammonia gave values from 3.42 to 3.53 for the molecular elevation of the boiling point. A second series of measurements gave values between 3.02 and 3.42, a third between 3.34 and 3.78. Omitting observations on solutions the concentrations, g/100 G, of which are above 10, the mean value of K for 20 observations is 3.39 as compared with 3.47 calculated above.

It would be unprofitable to attempt a discussion of the apparently erratic manner in which solutes—other than water—affect the boiling point of liquid ammonia. We shall content ourselves with noting that the effects of various solutes on the boiling point of ammonia simulate in a rough way their effects on the boiling point of water.

**Molecular Depression of the Freezing Point.** The cryoscopic constant of liquid ammonia calculated by means of the equation,  $K = 0.00198T^2/\lambda$ , in which  $T$  represents the absolute melting point and  $\lambda$  the heat of fusion, 81.5 cal./gram,<sup>2</sup> or 84.0 cal./gram,<sup>3</sup> is in

<sup>1</sup> Franklin and Kraus, *Am. Chem. J.*, 20, 836 (1898), 21, 8 (1899); Kraus, *J. Am. Chem. Soc.*, 30, 1197 (1908); Stock and Pohland, *Ber.*, 58, 657 (1925); Strain and Smith, *J. Am. Chem. Soc.*, 52, 5291 (1930).

<sup>2</sup> Eucken and Karwat, *Z. physik. Chem.*, 122, 478 (1924).

<sup>3</sup> Eucken and Donrath, *Z. physik. Chem.*, 124, 201 (1926).

the neighborhood of 9.3 to 9.0.

Direct measurements of the depression of the freezing point of four compounds dissolved in liquid ammonia have given the results shown in Table 3. The concentrations of the solutions in grams solute per 100 grams solvent are given under g/100 G, the molecular depression of the freezing point under K.<sup>4</sup>

TABLE 3.—Depression of the Freezing Point.

g/100 G	K	g/100 G	K	g/100 G	K	g/100 G	K
Water		Ethyl Alcohol		Sucrose		Sodium Nitrate	
0.70	9.8	0.51	11.1	3.03	8.6	0.45	12.7
1.58	9.7	1.09	10.0	4.10	8.8	0.85	10.9
3.00	9.7	4.98	9.5	5.42	9.9	1.90	10.3
6.08	9.7	9.14	9.2	7.27	10.3	3.69	10.1
11.64	9.9	15.90	8.6	9.07	9.2	6.41	10.7
20.8	10.7	30.4	7.9	10.82	10.4	14.4	11.0
26.5	11.3	41.5	7.3	14.5	10.0	19.0	11.3

An inspection of Table 3 shows that while water in the more dilute solutions gives values approximating 9.7 for the cryoscopic constant of liquid ammonia other solutes give rather widely varying results.

**Electrical Conductance of Liquid Ammonia Solutions.** In view of the remarkable manner in which liquid ammonia resembles water in its general physical and chemical properties it is not surprising to find that liquid ammonia solutions of a large variety of salts and other compounds are conductors of electricity. Next to water liquid ammonia is the best electrolytic solvent known in that it dissolves salts more abundantly and in greater variety than does any other solvent, excepting water, to form solutions which in general are excellent conductors of electricity. The conductances of some ninety-five compounds have been measured.<sup>5</sup>

In Figure 1 the molecular conductances of potassium iodide, potassium nitrate and sodium nitrate in liquid ammonia at  $-33^{\circ}$  and of potassium iodide in water at  $0^{\circ}$ ,  $18^{\circ}$  and  $25^{\circ}$ , in their dependence on dilution are shown graphically. The ordinates represent molecular conductances, the abscissas, the logarithms of the dilutions.

Franklin and Kraus, interpreting these curves in terms of the dissociation theory of Arrhenius, said that potassium nitrate at a concentration of five times normal in water solution at  $18^{\circ}$  is dissociated to the extent of something like sixty per cent and that

<sup>4</sup> Elliott, *J. Phys. Chem.*, **28**, 611 (1924).

<sup>5</sup> Franklin and Kraus, *Am. Chem. J.*, **23**, 277 (1900); *J. Am. Chem. Soc.*, **27**, 191 (1905); Franklin, *Z. physik. Chem.*, **69**, 272 (1909); F. A. Smith, Thesis, Stanford University, 1925; G. C. Griswold, Thesis, Stanford University, 1926; Strain, *J. Am. Chem. Soc.*, **49**, 1999 (1927).

<sup>6</sup> Sloan, *J. Am. Chem. Soc.*, **32**, 946 (1910).

dissociation approaches completion at a dilution of one thousand liters per molecule whereas in liquid ammonia solution at the same high concentration the salt is roughly ten per cent dissociated while the dilution necessary for bringing dissociation to approximate com-

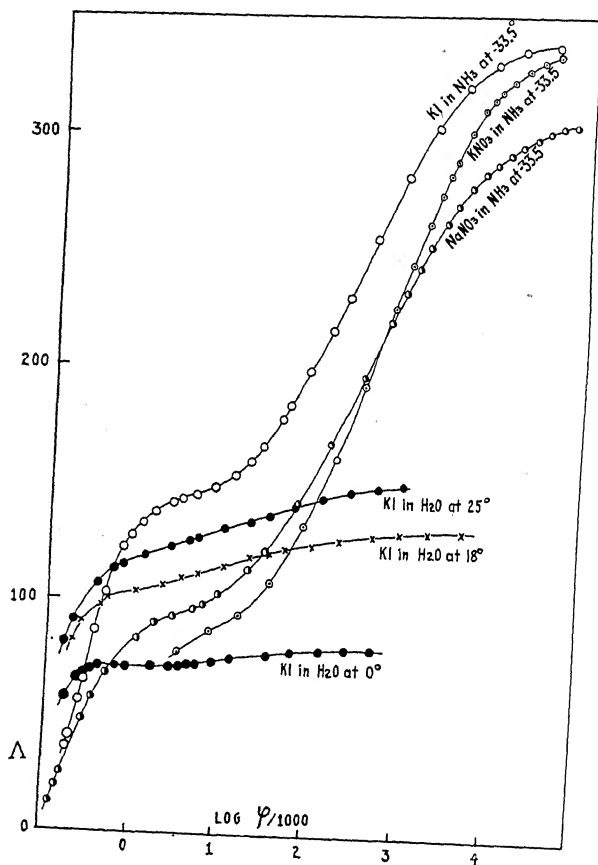


FIG. 1

pletion is around 100,000 liters per mole. One may say in view of these considerations that liquid ammonia is much the poorer ionizing solvent and explain the high molecular conductance of the dilute solutions on the assumption that the ions are much more mobile in liquid ammonia at  $-33^\circ$  than they are in water at  $18^\circ$ .

**Velocities of Ions in Liquid Ammonia.** We have explained the remarkably high molecular conductivity of dilute solutions of salts in liquid ammonia on the assumption that the ions, under a given potential slope, travel at a much greater speed in this solvent at

—33.4° than they do in water at laboratory temperature. In harmony with this explanation are the ion velocities measured by Franklin and Cady by the moving boundary method.<sup>7</sup>

These investigators found that under a potential slope of one volt per centimeter the following ions travel in centimeters per second at approximately the speeds indicated,  $\text{NH}_4 = 0.00135$ ,  $\text{K} = 0.00176$ ,  $\text{Na} = 0.00135$ ,  $\text{Ag} = 0.00111$ ,  $\text{NO}_3 = 0.00176$ , from which it will be seen that these ions travel from two and one-half to nearly three times as fast in liquid ammonia at —33° as they do in water at 18°.

**Optical Activity in Liquid Ammonia Solution.** In Table 4 are given the results of observations by Sherry<sup>8</sup> on some representative optically active compounds in solution in liquid ammonia. The measurements were made at 20°. The superscriptions,  $c$  and  $[\alpha]^D$ , represent respectively the concentration in grams of solute per 100 cc. of the solution and the specific rotation for sodium light.

TABLE 4.—Optically Active Compounds in Solution in Liquid Ammonia.

	$c$	$[\alpha]^D$	$c$	$[\alpha]^D$
Cane sugar *	8.2	76.0	48.8	73.6
Lactose .....	7.0	33.2	27.8	32.5
Raffinose .....	4.1	102.5	16.4	102.5
Glucose .....	3.5	56.1	27.8	55.3
Galactose .....	7.0	12.2	....	....
Fructose †	..	0	....	....
Asparagine .....	8.2	—26.9	32.8	—27.0
Amygdaline .....	4.1	—53.7	24.3	—53.7
Coniine hydrochloride ‡	4.1	10.3	8.2	10.1
Cocaine .....	3.5	—24.0	6.9	—24.0

\* In methylamine at  $c = 12.2$ ,  $[\alpha]^D = 75.8$ .

† Neither in ammonia nor in methylamine, nor in ethylamine does fructose show measurable optical activity.

‡ In sulfur dioxide at  $c = 7.7$ ,  $[\alpha]^D = 7.2$ .

**Liquid Ammonia as Solvent.** The earliest extensive investigations on the properties of liquid ammonia as a solvent were made by Gore,<sup>9</sup> who gives a list of 250 substances upon which experiments were made. Gore's investigations were undertaken for the purpose of ascertaining the general solvent properties of liquid ammonia and to detect any manifest chemical reactions between it and the various substances examined. The tests were made in Faraday tubes in which the ammonia, generated by heating ammoniated calcium chloride, was condensed by refrigeration and its own pressure on the substances to be studied.

Previous to the work of Gore, Weyl,<sup>10</sup> and Seely<sup>11</sup> and following

<sup>7</sup> Franklin and Cady, *J. Am. Chem. Soc.*, **26**, 499 (1904), *Proc. Amer. Assoc. Adv. Sci.*, **51**, 366 (1902); Kraus and Bray, *J. Am. Chem. Soc.*, **36**, 1361 (1913).

<sup>8</sup> Sherry, *J. Phys. Chem.*, **11**, 559 (1907).

<sup>9</sup> Gore, *Proc. Royal Soc. (London)*, **20**, 441 (1872); **21**, 140 (1873).

<sup>10</sup> Weyl, *Pogg. Ann.*, **121**, 601, 697 (1863); **123**, 350 (1864).

<sup>11</sup> Seely, *Chem. News*, **23**, 169 (1871); *J. Franklin Inst.*, **91**, 110 (1871).



Seely, Joannis<sup>12</sup> investigated the action of liquid ammonia on a limited number of substances, giving their attention especially to the blue solutions formed by dissolving the alkali metals in the liquid.

In complete ignorance of the work of their predecessors at the time their experiments were made, Cady<sup>13</sup> and Franklin and Kraus<sup>14</sup> took up the study of liquid ammonia with reference to its power as a solvent. Relieved by the commercial manufacturers of liquid ammonia from the necessity of preparing their solvent by the tedious method of Gore these investigators were able to study the behavior of liquid ammonia toward some 500 different substances under much more favorable conditions than were possible at the time Gore carried on his work.

The liquid ammonia used in making these solubility tests was the ordinary commercial liquid such as is furnished by the manufacturers to ice-making plants. Preliminary to carrying out the tests a quantity of liquid ammonia was drawn from the stock steel cylinder into a medium-sized Dewar tube after the manner described in detail in the appendix. The tests were then made by transferring to a small Dewar test tube, by means of a pipette (*Cf.* Fig. 2), a few cubic centimeters of the liquid, adding a small quantity of the substance under investigation and noting the extent of its solubility in the liquid. The general results obtained are summarized as follows.

*Elements.* The alkali metals dissolve readily and are recovered unchanged when the solvent is evaporated away. Metallic sodium has been obtained in the form of brilliantly lustrous dodecahedra by the slow evaporation of a solution of the metal.<sup>15</sup> The alkaline earth metals are soluble and are recovered as ammonates of the composition represented by the formula,  $M(NH_3)_6$ , on evaporating away the solvent.<sup>16</sup> Metallic magnesium is very slightly soluble.<sup>17</sup> Iodine, sulfur and phosphorus dissolve in liquid ammonia but at the same time enter into reaction with the solvent. Copper is acted upon by liquid ammonia in the presence of oxygen.

*Fluorides.* Of the fifteen fluorides tested by Gore three, potassium, silver and uranium fluorides, are reported as slightly soluble. The remainder are insoluble.

*Chlorides.* Among the chlorides which have been tested am-

<sup>12</sup> Joannis, *Compt. rend.*, 109, 900 (1889); 110, 238 (1890); 112, 337, 392 (1891); 113, 795 (1891); 114, 585 (1892); 115, 820 (1893); 116, 1370, 1518 (1893); 118, 713, 1149 (1894); 119, 357 (1894).

<sup>13</sup> Cady, *J. Phys. Chem.*, 1, 707 (1897).

<sup>14</sup> Franklin and Kraus, *Am. Chem. J.*, 20, 820 (1898).

<sup>15</sup> Unpublished observations.

<sup>16</sup> Kraus, *J. Am. Chem. Soc.*, 30, 660 (1908).

<sup>17</sup> Cottrell, *J. Phys. Chem.*, 18, 85 (1914).

monium chloride and beryllium chloride are very soluble, sodium chloride is moderately soluble, while, in general, other metallic chlorides are either insoluble or but slightly soluble. The chlorides of barium, strontium, calcium, zinc, manganese, cobalt, nickel, lead and silver, when added to liquid ammonia, react with the solvent. Considerable heat is generated as evidenced by the boiling of the solvent, the salts at the same time undergoing a sort of slaking process. The compact particles of the salt swell up and disintegrate, forming bulky masses, which in some cases are sufficiently soluble gradually to become crystalline. The product formed when calcium chloride was used was found to have the composition represented by the formula  $\text{CaCl}_2 \cdot 8\text{NH}_3$ . Others of these chlorides are well known to form ammonia addition products.

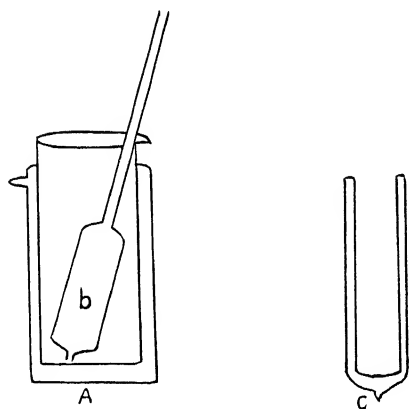


FIG. 2

*Bromides.* The metallic bromides are without exception distinctly more soluble than the chlorides. Of the limited number tested manganese bromide, ferrous bromide and ferric bromide are practically insoluble.

*Iodides.* Most of the metallic iodides are more or less soluble. The iodides of aluminum, silver, lead, mercury and bismuth are extremely soluble.

*Oxides and Hydroxides.* The metallic oxides and hydroxides are in general insoluble, though ordinary fused sodium hydroxide and potassium hydroxide are sufficiently soluble to impart an alkaline reaction to the liquid.

*Sulfates.* The sulfates, including ammonium sulfate, are quite insoluble.

*Sulfites.* The sulfites are in general insoluble.

*Sulfides.* Ammonium sulfide is readily soluble. The sulfides of

the alkali metals are but slightly soluble. The sulfides of arsenic are soluble. Other metallic sulfides so far tested are insoluble. Certain polysulfides are very soluble.

*Nitrates and Nitrites.* The nitrates in general are soluble as are also such nitrites as have been tested.

*Carbonates.* The carbonates, including ammonium carbonate, are insoluble.

*Phosphates.* The orthophosphates, pyrophosphates and metaphosphates are insoluble. Ammonium hypophosphite is moderately soluble.

*Arsenates and Antimonates.* Ammonium arsenate, copper arsenate and potassium pyroantimonate are insoluble.

*Cyanides.* The cyanides of the alkali metals, of mercury, silver and zinc are soluble. Certain of the double cyanides, such as potassium argenticyanide are soluble; others, such as the ferrocyanide and ferricyanide of potassium, are insoluble.

*Cyanates and Thiocyanates.* Potassium cyanate and silver cyanate are moderately soluble. The thiocyanates tested are extremely soluble.

*Hydrocarbons.* The paraffine hydrocarbons are practically insoluble at  $-33^{\circ}$ . Hexane and ammonia in a sealed tube at  $20^{\circ}$  are mutually soluble to a slight extent. The aromatic hydrocarbons are somewhat soluble. Benzene, which is distinctly soluble at  $-33^{\circ}$ , dissolves freely at  $20^{\circ}$ . The terpenes are practically insoluble.

*Alkyl and Aryl Halides.* The halogen substitution products of methane and ethane are all readily soluble. Derivatives of the higher hydrocarbons are slightly soluble. Chlorobenzene and p-chlorotoluene are slightly soluble.

*Alcohols and Phenols.* Methyl and ethyl alcohol, the propyl alcohols, the butyl alcohols and ordinary amyl alcohol are miscible with liquid ammonia. Cetyl alcohol is insoluble. The only two aromatic alcohols tested, namely benzyl alcohol and cinnamic alcohol, are miscible with ammonia. Ethylene glycol and glycerol are miscible, erythritol, dulcitol and mannitol are slightly soluble. Phenol, the cresols, all three dihydroxybenzenes and pyrogallol dissolve abundantly.

*Ethers.* Diethyl ether is miscible with ammonia at  $20^{\circ}$ , diamyl ether is slightly soluble, anisole and phenetole are miscible, benzyl-ethyl ether is slightly soluble.

*Aldehydes and Ketones.* Many aldehydes and ketones, aromatic as well as aliphatic, are very soluble. Aldehydes react with the solvent.

*Carboxylic Acids, Acid Amides and Acid Amidines.* Acetic acid is moderately soluble, valeric acid is slightly soluble, stearic acid is practically insoluble at  $-33^{\circ}$ , but is distinctly soluble at  $20^{\circ}$ , and

very soluble at 40°, while benzoic acid and the toluic acids dissolve freely. The dicarboxylic acids are insoluble. Acetamide and benzamide are abundantly soluble, palmitamide is distinctly soluble. Propionamidine and benzamidine, the only acid amidines which have been tested, are very soluble.

*Esters.* The esters in general are soluble. For example, ethyl carbonate, ethyl nitrate, ethyl acetate, phenyl acetate, methyl benzoate and ethyl tartrate are miscible with liquid ammonia. Ethyl caprylate and ethyl pelargonate are but slightly soluble. Many esters more or less rapidly undergo ammonolytic decomposition in solution in liquid ammonia.

*Nitriles, Isonitriles, Thiocyanates and Isocyanates.* Acetonitrile and propionitrile mix with ammonia in all proportions, palmitonitrile is slightly soluble, succinonitrile and o-toluenitrile are moderately soluble. Methyl and ethyl isocyanides, ethyl isocyanate, ethyl thiocyanate and ethyl isothiocyanate dissolve in all proportions.

*Amines.* With liquid ammonia at 20°, 0° and —33°, methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, normal propylamine and isoamylamine are miscible in all proportions while tri-n-propylamine diisoamylamine and triisoamylamine form two layers. Triethylamine and diisopropylamine are miscible with liquid ammonia at 20° and form two layers at 0°. Hexylamine is miscible at 20° and forms two layers at —33°.

*Nitro Compounds.* Nitro derivatives of the hydrocarbons, aromatic as well as aliphatic, are soluble, some of them abundantly so.

*Sulfonic Acids.* The aromatic sulfonic acids are generally soluble as well as are also many of their metallic salts.

*Heterocyclic Compounds.* Certain heterocyclic compounds, such as pyridine, quinoline, indole, pyrrole, imidazole and thiophene, dissolve abundantly in liquid ammonia. Others, for example, isoquinoline and tetrazole, dissolve sparingly.

## CHAPTER II.

### REACTIONS IN LIQUID AMMONIA.

Reactions take place in liquid ammonia solutions with all the facility which characterizes the more familiar reactions in water. Here we shall concern ourselves with certain metathetic reactions between salts and with the action of ammonium salts on metals, metallic hydroxides, oxides, amides, imides and nitrides, leaving other important reactions to be discussed in various connections later.

**Reactions Between Salts.** A consideration of the remarkable manner in which liquid ammonia resembles water led Franklin and Kraus<sup>1</sup> to inquire whether ordinary metathetic reactions may take place in the former solvent as they do in the latter. As a matter of fact, they found this to be the case though the reactions in liquid ammonia by no means always run parallel to those in water nor is the variety of reactions between salts in liquid ammonia nearly so great as in water. None of the familiar reactions involving the precipitation of sulfates, carbonates, phosphates and oxalates are possible in liquid ammonia solution for the simple reason that no salts of these acids are soluble in this solvent.

Most metallic chlorides are insoluble or but slightly soluble in liquid ammonia. Accordingly it was found that the addition of a solution of sodium chloride to a solution of calcium nitrate gives a precipitate of calcium chloride,  $2\text{NaCl} + \text{Ca}(\text{NO}_3)_2 = \text{CaCl}_2 + 2\text{NaNO}_3$ , and that the chlorides of barium, strontium, magnesium, zinc, cadmium, manganese, cobalt and nickel are obtained as precipitates when to the solution of the respective nitrates either sodium chloride or ammonium chloride is added. The chlorides of lithium, potassium, lead, silver and copper, being somewhat soluble, separate as crystalline precipitates from solutions which are not too dilute.

Ammonium bromide precipitates bromides of the alkaline earth metals, manganese, cadmium, cobalt and nickel from solutions of the respective nitrates. For the precipitation of the bromides of magnesium and zinc higher concentrations are necessary. The bromides of lithium, lead and silver, being distinctly soluble, separate only from rather highly concentrated solutions.

<sup>1</sup> Franklin and Kraus, *Am. Chem. J.*, 21, 1 (1899).

Ammonium iodide precipitates the slightly soluble iodides of calcium, strontium, barium and cadmium from solutions of the nitrates of these metals.

Ammonium chromate and ammonium borate, which are slightly soluble in liquid ammonia, give precipitates when added to solutions of the above-enumerated metallic nitrates.

The reactions brought about by the addition of hydrogen sulfide (ammonium sulfide) to solutions of a number of metallic salts are of particular interest. Colorless metallic sulfides are precipitated when the precipitant is added to solutions of the nitrates of calcium, strontium, barium, magnesium, zinc, manganese, nickel and cadmium. The precipitate formed by adding ammonium sulfide to cupric nitrate is yellowish brown, the cobalt precipitate is pink, while the salts of lead, silver, mercury and bismuth give black precipitates. Excepting the magnesium compound, which has the composition,  $2\text{MgS} \cdot (\text{NH}_4)_2\text{S} \cdot x\text{NH}_3$ , in which  $x$  is either 9 or 10, the composition of these precipitates is unknown, though doubtless the lead, silver, mercury and bismuth precipitates are the familiar sulfides.

These metathetic reactions were carried out in a purely qualitative way in vacuum-jacketed beakers open to the atmosphere. For example, a precipitate of ammoniated calcium chloride is obtained when a solution of ammonium chloride is transferred from a vacuum-jacketed beaker *A* (Fig. 2, p. 21), by means of a pipette *B* to a second beaker *C* containing a solution of calcium nitrate.

Especially interesting is the formation of a precipitate of barium bromide when a liquid ammonia solution of silver bromide is added to a solution of barium nitrate. The equation,  $\text{BaBr}_2 + 2\text{AgNO}_3 = 2\text{AgBr} + \text{Ba}(\text{NO}_3)_2$ , read from left to right, represents what takes place in water solution. The reaction represented by the same equation read from right to left takes place in liquid ammonia. A precipitate of ammoniated barium bromide separates from solutions which are not too dilute.

This reaction has been carried out quantitatively in a two-legged reaction tube

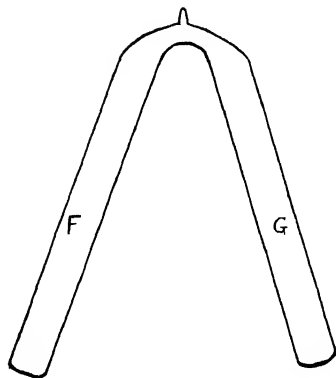
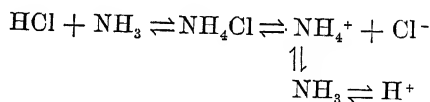
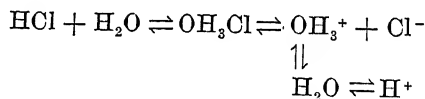


FIG. 3

containing liquid ammonia solutions of barium nitrate and silver bromide in the respective legs. When solution is poured from *F* into *G*, or from *G* into *F*, a precipitate of barium bromide is formed. Analysis of the precipitate showed it to have the composition represented by the formula,  $\text{BaBr}_2 \cdot 8\text{NH}_3$ . In a similar manner a precipitate of barium iodide is formed when liquid ammonia solution of silver iodide and barium nitrate or barium thiocyanate are brought together. A saturated solution of silver chloride gives with a saturated solution of barium nitrate a slight precipitate of barium chloride.

**The Action of Ammonium Salts as Acids.** Ammonium salts in liquid ammonia solution attack many metals and react with metallic hydroxides and oxides in a manner closely resembling the action of acids in water solution excepting that the reactions in liquid ammonia are much more sluggish than are those in water.

When hydrogen chloride is dissolved in water a solution is formed which shows the properties of a strong acid, since in accordance with the electrolytic dissociation theory of Arrhenius the acid is highly ionized as represented by the equation,  $\text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^-$ , in which equilibrium is displaced far to the right. On the other hand in liquid ammonia solution hydrogen chloride is present in the form of its ammonium salt which is dissociated into ammonium ions and chlorine ions. It is reasonable to assume that the solution of hydrochloric acid in water and in liquid ammonia respectively results in fundamentally analogous equilibria. One may therefore write the equations,



to represent the equilibria in water and liquid ammonia solutions of hydrochloric acid and say that the hydrogen ion concentration is greater in the former solvent than in the latter, or rather perhaps since according to Brønsted<sup>2</sup> the hydrogen-ion (proton) concentration in both solutions is too utterly small to be of any kinetic significance, one may say that the escaping tendency of the proton from the oxonium ion is greater than it is from the ammonium ion.

**Action on Metals.** Divers<sup>3</sup> found many years ago that potassium, sodium, magnesium, zinc and cadmium dissolve in the highly

<sup>2</sup> Brønsted, *Chem. Rev.*, **5**, 240 (1928).

<sup>3</sup> Divers, *Proc. Roy. Soc. (London)*, **21**, 109 (1875); *Phil. Trans.*, **163**, 368 (1874); Franklin, *J. Am. Chem. Soc.*, **27**, 822 (1908).

concentrated solution of ammonium nitrate formed by the deliquescence of the salt in contact with dry ammonia gas at 0°.<sup>4</sup>

According to Divers the solution of these metals takes place with the reduction of a portion of the ammonium nitrate to ammonium nitrite and, excepting in the case of magnesium, without the evolution of hydrogen.

Franklin and Kraus,<sup>5</sup> observed that potassium, sodium and calcium in liquid ammonia solution react with ammonium salts, metallic sodium with ammonium chloride, for example, in accordance with the equation,  $\text{Na} + \text{NH}_4\text{Cl} = \text{NaCl} + \text{H} + \text{NH}_3$ , to form sodium chloride and hydrogen.

According to Browne and Houlehan<sup>6</sup> ammonium azide in liquid ammonia solution reacts readily with lithium, potassium, sodium, calcium and magnesium to form the respective metallic azides,  $\text{LiN}_3$ ,  $\text{KN}_3$ ,  $\text{NaN}_3$ ,  $\text{CaN}_6 \cdot x\text{NH}_3$  and  $\text{MgN}_6 \cdot x\text{NH}_3$ , together, in each case, with the evolution of approximately equivalent amounts of hydrogen. They observed furthermore that zinc is slowly attacked by the ammonium azide solution; aluminum and tin, however, not at all.

Franklin,<sup>7</sup> prepared the ammonated salts represented by the formulas,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{NH}_3$  and  $\text{MgI}_2 \cdot 6\text{NH}_3$ , by the action of liquid ammonia solutions of ammonium nitrate and ammonium iodide respectively on metallic magnesium. Whether or not ammonium nitrite is also formed by the action of metallic magnesium on ammonium nitrate was not determined.

Davis, Olmstead and Lundstrom<sup>8</sup> report that liquid ammonia solutions of ammonium nitrate and of ammonium thiocyanate attack iron and steel with considerable rapidity.

Observations by Bergstrom<sup>9</sup> on the action of liquid ammonia solutions of ammonium salts on metals may be summarized as follows:

Amalgamated aluminum dissolves readily in solutions of ammonium nitrate. Metallic manganese is converted into the ammonated bromide,  $\text{MnBr}_2 \cdot 6\text{NH}_3$ , by the action of ammonium bromide and is rather rapidly attacked by ammonium nitrate and by ammonium cyanide, very slowly by the slightly soluble ammonium chromate. Lanthanum and cerium dissolve in ammonium iodide solutions to form the readily soluble iodides of the respective formulas,  $\text{LaI}_3 \cdot x\text{NH}_3$  and  $\text{CeI}_2 \cdot x\text{NH}_3$ . A sparingly soluble ammonated

<sup>4</sup> The vapor pressure of this solution—containing about 76 per cent ammonium nitrate and 24 per cent ammonia—which came later to be known as Divers' liquid— is 360 mm. at 0°.

<sup>5</sup> Franklin and Kraus, *Am. Chem. J.*, **23**, 305 (1900).

<sup>6</sup> Browne and Houlehan, *J. Am. Chem. Soc.*, **33**, 1742 (1911).

<sup>7</sup> Franklin, *J. Am. Chem. Soc.*, **35**, 1454 (1913).

<sup>8</sup> Davis, Olmstead and Lundstrom, *J. Am. Chem. Soc.*, **43**, 1583 (1921).

<sup>9</sup> Bergstrom, *J. Phys. Chem.*, **29**, 160 (1925); *J. Am. Chem. Soc.*, **50**, 657 (1928).



cerium bromide,  $\text{CeBr}_3 \cdot x\text{NH}_3$ , is obtained by the action of ammonium bromide solution on metallic cerium, a slightly soluble cadmium nitrate hexammonate,  $\text{Cd}(\text{NO}_3)_2 \cdot 6\text{NH}_3$ , by the action of ammonium nitrate solution on metallic cadmium. Ammonated salts of the formulas,  $\text{Fe}(\text{NO}_3)_2 \cdot 6\text{NH}_3$ ,  $\text{FeBr}_2 \cdot 6\text{NH}_3$ , and  $(\text{NH}_4)_2\text{Fe}(\text{CN})_6 \cdot 2\text{NH}_3$ , are formed by the slow action of ammonium nitrate, ammonium bromide and ammonium cyanide respectively on metallic iron. These three salts are but slightly soluble in liquid ammonia. Ammonium nitrate reacts very slowly with metallic cobalt with the result that a pinkish-red solution, presumably of cobalt nitrate, is formed. A slightly soluble nickel nitrate hexammonate,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$ , is obtained by the action of ammonium nitrate solution on metallic nickel. Metallic beryllium dissolves in liquid ammonia solutions of the chloride, bromide, iodide, azide, cyanide and thiocyanate of ammonium with the evolution of hydrogen and the formation, presumably, of the beryllium salts of the respective acids. The solutions of the normal salts thus formed dissolve further amounts of metallic beryllium to form basic salts. (Cf. p. 27.)

It has been shown<sup>10</sup> that at elevated temperatures ammonium chloride attacks copper, silver, nickel and iron much more rapidly than does dry or even moist hydrochloric acid.

**Action on Metallic Hydroxides and Oxides.** Divers<sup>11</sup> showed that the hydroxides of sodium and potassium and the oxides of calcium, magnesium, zinc, cadmium, lead, copper and mercury dissolve rather freely in Divers' liquid which, it will be recalled, is a highly concentrated solution of ammonium nitrate in liquid ammonia.

It has frequently been observed in this laboratory that metallic hydroxides and oxides, which are practically insoluble in liquid ammonia, dissolve readily in solutions of ammonium salts. The action of ammonium chloride solution on sodium hydroxide, for example, has been carried out in the following manner.

The one leg of the familiar reaction tube (Fig. 3, p. 25) contains a few pieces of sodium hydroxide covered with liquid ammonia containing a minute amount of phenolphthalein, the other a solution of ammonium chloride. As has been stated, the aquo base is almost entirely insoluble. None the less it is sufficiently soluble<sup>12</sup> to give the characteristic red color to the phenolphthalein solution. On pouring a minute quantity of the ammonium chloride solution into the first leg of the tube the red color is instantly discharged. Soon, however, and more quickly with shaking, the red color reappears. Again upon adding ammonium chloride solution the color disappears. With the addition of excess of ammonium chloride all the sodium hydroxide goes into solution as sodium chloride. The

<sup>10</sup> Hofmann, Hartmann and Nagel, *Ber.*, **58**, 808 (1925); Hofmann and Hartmann, *Ber.*, **58**, 2466 (1925).

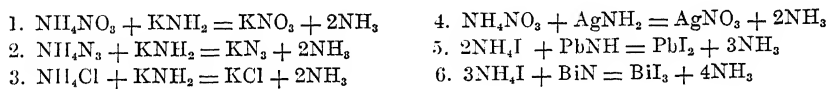
<sup>11</sup> Divers, *Proc. Roy. Soc. (London)*, **21**, 109 (1875); *Phil. Trans.*, **163**, 368 (1874).

<sup>12</sup> A saturated solution of sodium hydroxide in liquid ammonia at 0° contains something like 6 to 8 mg. of the aquo base to 100 cc. of the solution.

reaction involved takes place in accordance with the equation,  $\text{NaOH} + \text{NH}_4\text{Cl} = \text{NaCl} + \text{H}_2\text{O} + \text{NH}_3$ , and is identical in principle with the reaction involved in the interaction of hydrochloric acid and sodium hydroxide in water solution. Removing the solution from the reaction tube, evaporating away the solvent and gently igniting the residue to drive off water and excess of ammonium chloride, a quantity of sodium chloride equivalent to the sodium hydroxide used is obtained.<sup>13</sup>

Even in water solution the acid properties of ammonium salts are occasionally in evidence, as for example in the well-known cases of the solubility of metallic zinc and magnesium and of certain metallic oxides, hydroxides and carbonates in aqueous solutions of ammonium salts. Ammonium chloride in solution in water functions as an acid in the so-called dry cell. Especially interesting in this connection, as will be discussed in detail in a subsequent chapter, is the conversion of the mercury ammonium compounds into normal mercuric salts by the action of ammonium salts in aqueous solution. (*Cf.* Chapter IX.)

**Action on Metallic Amides, Imides and Nitrides.** Ammonium salts in liquid ammonia solution react with metallic amides, imides and nitrides. Examples of such reactions are represented by the equations,



The reactants as well as the reaction products formulated in equations 1 and 2 are soluble in liquid ammonia. Potassium chloride, being slightly soluble, appears as a precipitate when potassium amide is neutralized by the action of ammonium chloride, equation 3. Silver amide, lead imide and bismuth nitride, which are insoluble, go into solution as silver nitrate, lead iodide and bismuth iodide respectively as represented by the fourth, fifth and sixth equations.

<sup>13</sup> Unpublished observations.

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## CHAPTER III.

### THE NITROGEN SYSTEM OF BASES, ACIDS AND SALTS.

The ordinary oxygen bases, acid and salts, the basic oxides and the acid anhydrides may be looked upon as derivatives of water or in the words of Thales of Miletus, as water variously metamorphosed. Thus it is reasonable to say that a derivative of water is obtained when potassium hydroxide is formed by the action of metallic potassium on water, that a divalent calcium atom takes the place of one atom of hydrogen in each of two molecules of water when calcium acts on water to form calcium hydroxide, that water becomes hypochlorous acid when one of the hydrogen atoms of the mother substance is replaced by unipositive or hypochlorous acid chlorine. The molecule of nitric acid may be regarded as a molecule of water in which one of the hydrogen atoms is replaced by the  $\text{NO}_2$  group, or it may be said to be made up of three molecules of water in which five of the six hydrogen atoms are replaced by pentapositive or nitric acid nitrogen.

When both hydrogen atoms in water are replaced by metal atoms a basic oxide results, when replaced by non-metals or acid-forming groups an acid anhydride is formed. An example of the former is potassium oxide, two examples of the latter are hypochlorous anhydride,  $\text{Cl-O-Cl}$ , and nitrogen pentoxide,  $\text{O}_2\text{N-O-NO}_2$ .

The oxygen salts may be said to be derivatives of water in which part of the hydrogen is replaced by a metal or a base-forming group while the place of the other portion is occupied by an acid-forming element or radical. Thus a molecule of potassium hypochlorite,  $\text{K-O-Cl}$ , may be regarded as a molecule of water the one hydrogen atom of which is replaced by a base-forming potassium atom, the other by an acid-forming hypochlorous acid chlorine atom; a molecule of potassium nitrate,  $\text{K-O-NO}_2$ , as a molecule of water in which half of the hydrogen is substituted by a potassium atom, the other half by the  $\text{NO}_2$  group.

The oxygen bases, acids and salts, the alcohols, aldehydes, and in general all compounds containing oxygen, may be looked upon as derivatives of water and as such to constitute the oxygen system of compounds.

The many properties held in common by oxygen and nitrogen and especially the very striking way in which liquid ammonia resembles water both in its physical and chemical properties leads us

at once to inquire whether ammonia may be regarded as the parent substance from which the many known nitrogen compounds are analogously derived.

On the assumption that this close resemblance between water and liquid ammonia extends to their respective derivatives it follows that the metallic amides and imides, which are related to ammonia as the metallic hydroxides are related to water, may be regarded as bases of the nitrogen system while the metallic nitrides are basic nitrides corresponding to the basic oxides of the oxygen system. The amides of the electronegative or acid-forming elements, together with their partially deammonated products are acids of the nitrogen system, while the final deammonation products, the acid nitrides, are the nitrogen analogs of the acid anhydrides.

Examples of oxygen bases, acids and salts, basic oxides and acid anhydrides together with their nitrogen analogs are given in Table 5.

TABLE 5.—*Comparison Between Oxygen Bases, Acids and Salts, Basic Oxides and Acid Anhydrides with Their Nitrogen Analogs.*

Metallic Hydroxides and Oxides	Metallic Amides, Imides and Nitrides
Lithium hydroxide .....LiOH	Lithium amide .....LiNH <sub>2</sub>
Lithium oxide .....Li <sub>2</sub> O	Lithium imide .....Li <sub>2</sub> NH
Calcium hydroxide ...Ca(OH) <sub>2</sub>	Lithium nitride .....Li <sub>3</sub> N
Calcium oxide .....CaO	Calcium amide .....Ca(NH <sub>2</sub> ) <sub>2</sub>
Hydrous aluminium oxide .....Al <sub>2</sub> O <sub>3</sub> .xH <sub>2</sub> O	Calcium imide .....[CaNH]
Aluminium oxide .....Al <sub>2</sub> O <sub>3</sub>	Calcium nitride .....Ca <sub>3</sub> N <sub>2</sub>
Silver hydroxide .....[AgOH]	Ammonous aluminium nitride .....AlN.xNH <sub>3</sub>
Silver oxide .....Ag <sub>2</sub> O	Aluminium nitride .....AlN
Lead hydroxide .....Pb(OH) <sub>2</sub>	Silver amide .....AgNH <sub>2</sub>
Lead oxide .....PbO	Silver imide .....[Ag <sub>2</sub> NH]
Mercuric hydroxide .[Hg(OH) <sub>2</sub> ]	Silver nitride .....[Ag <sub>3</sub> N]
Mercuric oxide .....HgO	Lead amide .....[Pb(NH <sub>2</sub> ) <sub>2</sub> ]
	Lead imide .....PbNH
	Lead nitride .....[Pb <sub>2</sub> N <sub>2</sub> ]
	Mercuric amide ... (Hg(NH <sub>2</sub> ) <sub>2</sub> )
	Mercuric imide .....(HgNH)
	Mercuric nitride .....Hg <sub>3</sub> N <sub>2</sub>
<i>Acids and Acid Oxides</i>	
Ortho carbonic acid ..((HO) <sub>4</sub> C)	<i>Acids and Acid Nitrides</i>
Carbonic acid .....((HO) <sub>2</sub> CO)	Carbon tetramide ..[(H <sub>2</sub> N) <sub>4</sub> C]
	Guanidine .....(H <sub>2</sub> N) <sub>2</sub> C-NH
	Cyanamide .....H <sub>2</sub> NCN
	Dicyanimide .....HN(CN) <sub>2</sub>

Carbon dioxide .....	$\text{CO}_2$	Carbonic nitride .....	$(\text{C}_3\text{N}_4)_x$
Nitric acid .....	$\text{HONO}_2$	Hydrazoic acid .....	$\text{HN}=\text{N}=\text{N}$
Nitrous acid .....	$(\text{HONO})$	Triazene .....	$(\text{HN}-\text{N}-\text{NH}_2)$
Orthophosphoric acid .....	$(\text{HO})_3\text{PO}$	Phosphoric nitride-amide .....	$(\text{H}_2\text{N})_2\text{PN}$
Metaphosphoric acid .....	$\text{HOPO}_2$	Phospham .....	$\text{HNPN}$
Phosphoric anhydride .....	$\text{P}_2\text{O}_5$	Phosphoric nitride .....	$\text{P}_3\text{N}_5$
Hypochlorous acid .....	$\text{HOCl}$	Monochloramine .....	$\text{H}_2\text{NCl}$
		Dichloramine .....	$\text{HNCl}_2$
Chlorine oxide .....	$\text{Cl}_2\text{O}$	Chlorine nitride .....	$\text{Cl}_3\text{N}$
Acetic acid .....	$\text{CH}_3\text{COOH}$	Acetamidine ...	$\text{CH}_3\text{C}(\text{NH})\text{NH}_2$
Acetic anhydride ..	$(\text{CH}_3\text{CO})_2\text{O}$	Acetonitrile .....	$\text{CH}_3\text{CN}$

*Salts*

Monopotassium carbonate .....	$\text{HKCO}_3$
Dipotassium carbonate ..	$\text{K}_2\text{CO}_3$
Potassium nitrate .....	$\text{KNO}_3$
Potassium acetate...	$\text{CH}_3\text{COOK}$

*Salts*

Dipotassium guanidine .....	$\text{K}_2\text{H}_3\text{CN}_3$
Monopotassium cyanamide .....	$\text{KHCN}_2$
Dipotassium cyanamide ..	$\text{K}_2\text{CN}_2$
Potassium dicyanamide ..	$\text{KC}_2\text{N}_3$
Potassium azide .....	$\text{KNN}_2$
Potassium acetamidine .....	$\text{CH}_3\text{C}(\text{NH})\text{NHK}$

Formulas in brackets represent unknown compounds, those in parentheses compounds known in the form of derivatives only.

Proceeding now on the assumption that the formal analogies thus developed are real it follows that as the metallic hydroxides react with acids to form salts so one would expect to find their nitrogen analogs capable of entering into reactions in a closely similar manner. As a matter of fact many such reactions have been observed by the writer and his students. For example, just as potassium hydroxide and carbonic acid interact in water solution to form potassium carbonate and water,  $2\text{KOH} + \text{H}_2\text{CO}_3 = \text{K}_2\text{CO}_3 + 2\text{H}_2\text{O}$ , so, in liquid ammonia solution, potassium amide acts on cyanamide in accordance with the equation,  $2\text{KNH}_2 + \text{H}_2\text{CN}_2 = \text{K}_2\text{CN}_2 + 2\text{NH}_3$ , to form potassium cyanamide and ammonia. In the one case a base, an acid and a salt of the oxygen system are involved, in the other a base, an acid and a salt of the nitrogen system.

Potassium amide, cyanamide and monopotassium cyanamide<sup>1</sup> form electrically conducting solutions when dissolved in liquid ammonia just as is familiarly known to be the case with water solutions of potassium hydroxide, carbonic acid and potassium carbonate.

Bases, acids and salts of the nitrogen system, again of course in

<sup>1</sup> Dipotassium cyanamide is insoluble in liquid ammonia.

solution in liquid ammonia, bring about the same reciprocal color changes of indicators which are so well known to characterize the action of bases and acids in water solution.

Following is a description of a striking experiment illustrative of this statement. A liquid ammonia solution of a minute amount of phenolphthalein contained in the middle branch of the three-legged reaction tube shown in Figure 4,

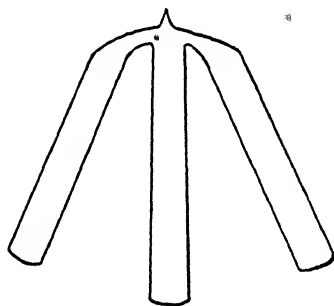


FIG. 4

is quite as colorless as a neutral aqueous solution of the same indicator. A single drop of a dilute solution of potassium amide poured over from one of the side branches into the phenolphthalein solution develops instantly the red color characteristic of aqueous alkaline solutions of phenolphthalein. Addition of dicyanamide solution from the second side tube discharges the color quite as sharply as does an ordinary acid in water solution. Equivalent quantities of potassium amide and dicyanamide react to form the potassium salt,  $\text{KC}_2\text{N}_3$ , which crystallizes from the properly concentrated and cooled solutions. Using triphenylmethane instead of phenolphthalein as indicator in this experiment the operator has in his hands a system in which no compounds of oxygen are present.

Metallic amides, imides and nitrides are precipitated from liquid ammonia solutions of certain metallic salts by the action of potassium amide just as metallic hydroxides and oxides are precipitated from water solutions by the action of potassium hydroxide. Examples of such reactions are given in Table 6.

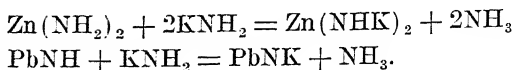
TABLE 6.—Action of Bases on Salts.

In Liquid Ammonia	In Water
$\text{AgNO}_3 + \text{KNH}_2 = \text{AgNH}_2 + \text{KNO}_3$	$2\text{AgNO}_3 + 2\text{KOH} = \text{Ag}_2\text{O} + 2\text{KNO}_3 + \text{H}_2\text{O}$
$\text{PbI}_2 + 2\text{KNH}_2 = \text{PbNH}_2 + \text{NH}_3 + 2\text{KI}$	$\text{Pb}(\text{NO}_3)_2 + 2\text{KOH} = \text{Pb}(\text{OH})_2 + 2\text{KNO}_3$
$3\text{HgI}_2 + 6\text{KNH}_2 = \text{Hg}_3\text{N}_2 + 4\text{NH}_3 + 6\text{KI}$	$\text{HgCl}_2 + 2\text{KOH} = \text{HgO} + 2\text{KCl} + \text{H}_2\text{O}$
$\text{BiI}_3 + 3\text{KNH}_2 = \text{BIN} + 3\text{KI} + 2\text{NH}_3$	$\text{Bi}(\text{NO}_3)_3 + 3\text{KOH} = \text{Bi}(\text{OH})_3 + 3\text{KNO}_3$
$\text{NaNO}_3 + \text{KNH}_2 = \text{NaNH}_2 + \text{KNO}_3$	
$\text{Ba}(\text{NO}_3)_2 + 2\text{KNH}_2 = \text{Ba}(\text{NH}_2)_2 + 2\text{KNO}_3$	
$3\text{TlNO}_3 + 3\text{KNH}_2 = \text{Tl}_3\text{N} + 3\text{KNO}_3 + 2\text{NH}_3$	

Clearly the action of potassium amide on metallic salts in liquid ammonia solution resembles in a very striking way the familiar

action of potassium hydroxide on the same salts in water solution.

Finally just as certain amphoteric metallic hydroxides dissolve in an excess of potassium hydroxide in water solution so many metallic amides and imides react with potassium amide in liquid ammonia solution, zinc amide and lead imide for example, as represented by the equations,



The reactions represented by these equations closely resemble those involved in the action of aqueous potassium hydroxide on the hydroxides of zinc and lead. Many similar reactions have been studied. (*Cf.* Chapter VII.)

Excepting the oxides of nitrogen, which because of the dominantly negative character of oxygen, must be counted as members of the oxygen system, all other compounds of nitrogen<sup>2</sup> may be looked upon as derivatives of ammonia and as such to constitute an ammonia or nitrogen system of compounds. We shall learn the full significance of this general statement as we proceed.

<sup>2</sup> In view of the fact that fluorine is the most powerfully negative of all the elements Ruff's compounds,  $\text{F}_3\text{N}$ ,  $\text{F}_2\text{NH}$ , and  $\text{FNH}_2$ , are to be regarded as belonging to a fluorine or hydrogen fluoride system of compounds. [*Cf.* Franklin, *J. Am. Chem. Soc.*, 46, 2137 (1924).]

## CHAPTER IV.

### NOMENCLATURE.

Before proceeding to a detailed discussion of the bases, acids and salts and other classes of compounds belonging to the nitrogen system it is desirable to outline a system of nomenclature by means of which we may indicate clearly and concisely by suitable names the compounds concerned and the reactions in which they take part.

**Ammono Bases, Ammono Acids and Ammono Salts.** Since the bases, acids and salts of the nitrogen system may be regarded as derivatives of ammonia it becomes reasonable to adopt the prefix ammono for use in distinguishing these compounds from their oxygen analogs. Accordingly potassium amide,  $\text{KNH}_2$ , calcium amide,  $\text{Ca}(\text{NH}_2)_2$ , lithium imide,  $\text{Li}_2\text{NH}$ , and aluminum amide-imide,  $\text{Al}(\text{NH})\text{NH}_2$ , are ammono bases, cyanamide,  $\text{H}_2\text{NCN}$ , is an ammono carbonic acid, calcium cyanamide,  $\text{CaNCN}$  is an ammonocarbonate of calcium, acetamidine,  $\text{CH}_3\text{C}(\text{NH})\text{NH}_2$ , is an ammono acetic acid and the compound represented by the formula  $\text{C}_6\text{H}_5\text{C}(\text{NH})\text{NHK}$ , is a potassium ammonobenzoate.

**Aquo Bases, Aquo Acids and Aquo Salts.** When it becomes necessary to distinguish by name between the bases, acids and salts of the oxygen and nitrogen systems we shall speak of members of the former system as aquo bases, aquo acids and aquo salts. Potassium hydroxide for example will sometimes be referred to as an aquo base,<sup>1</sup> nitric acid as aquo nitric acid and potassium nitrate as potassium aquonitrate. The formulas,  $\text{C}_6\text{H}_5\text{COOH}$  and  $\text{C}_6\text{H}_5\text{COOK}$ , represent respectively an aquo benzoic acid and a potassium aquobenzoate.

**Aquo-Ammono Acids, Aquo-Ammono Salts.** We shall find that there are many acids and salts known which must be looked upon as belonging at the same time to both the oxygen and nitrogen systems. Such mixed acids and salts will be called aquo-ammono acids and aquo-ammono salts respectively. Acetamide, a tautomeric compound which may be represented by either of the formulas,  $\text{CH}_3\text{CONH}_2$  or  $\text{CH}_3\text{C}(\text{NH})\text{OH}$ , is an example of an aquo-ammono acetic acid. The potassium derivative of acetamide is a potassium aquo-ammono-acetate to which any one of the formulas,  $\text{CH}_3\text{CONHK}$ ,

<sup>1</sup> No names are in use which indicate that the metallic hydroxides are bases. Since potassium hydroxide and potassium amide are both bases we shall sometimes call the first potassium aquo base, the second potassium ammono base.



$\text{CH}_3\text{C}(\text{OH})\text{NK}$  or  $\text{CH}_3\text{C}(\text{OK})\text{NH}$ , may be given or perhaps even rather the formula,  $\text{CH}_3\text{CON}(\text{HK})$ , which represents neither the hydrogen nor the potassium as attached directly to either the oxygen or the nitrogen. Cyanic acid,  $\text{OC}\cdot\text{NH}$ ,  $\text{NC}\cdot\text{OH}$ , and urea,  $\text{H}_2\text{N}\cdot\text{CO}\cdot\text{NH}_2$ , are aquo-ammono carbonic acids. Nitramide, to which any one of the formulas,  $\text{H}_2\text{N}\cdot\text{NO}_2$ ,  $\text{HN}\cdot\text{NO}\cdot\text{OH}$  or  $\text{N}\equiv\text{N}(\text{OH})_2$ , may be ascribed, is an aquo-ammono nitric acid. Amido sulfuric acid,  $\text{H}_2\text{N}\cdot\text{SO}_2\cdot\text{OH}$ , and sulfamide,  $\text{H}_2\text{N}\cdot\text{SO}_2\cdot\text{NH}_2$ , are aquo-ammono sulfuric acids.

Only one compound, so-called Millon's base,  $\text{Hg}\cdot\text{N}\cdot\text{Hg}\cdot\text{OH}\cdot x\text{H}_2\text{O}$ , is known which may be looked upon as a mixed aquo-ammono base and even this product is probably a mixture and not a definite compound. (Chapter IX.)

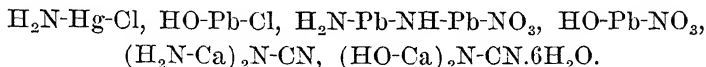
**Thio Acids, Aquo-Thio Acids, Ammono-Thio Acids and Aquo-ammono-Thio Acids.** The formulas, (1)  $\text{C}(\text{SH})_4$ , (2)  $\text{SC}(\text{SH})_2$ , (3)  $\text{SC}(\text{SH})\text{OH} \rightleftharpoons \text{OC}(\text{SH})_2$ , (4)  $\text{SC}(\text{OH})_2 \rightleftharpoons \text{OC}(\text{SH})\text{OH}$ , (5)  $\text{SC}(\text{SH})\text{NH}_2 \rightleftharpoons \text{HNC}(\text{SH})_2$ , (6)  $\text{HNCS} \rightleftharpoons \text{HSCN}$ , (7)  $\text{SC}(\text{NH}_2)_2 \rightleftharpoons \text{HNC}(\text{SH})\text{NH}_2$ , (8)  $\text{SC}(\text{OH})\text{NH}_2 \rightleftharpoons \text{OC}(\text{SH})\text{NH}_2 \rightleftharpoons \text{HNC}(\text{SH})\text{OH}$ , represent carbonic acids, known in the free state or in the form of salts or esters, which may be named as follows, (1) and (2) thio carbonic acids, (3) and (4) aquo-thio carbonic acids, (5), (6) and (7) thio-ammono carbonic acids and (8) an aquo-thio-ammono carbonic acid.

The two acids represented by the formulas,  $\text{CH}_3\text{CSOH} \rightleftharpoons \text{CH}_3\cdot\text{COSH}$  and  $\text{CH}_3\text{CSSH}$ , known as thio acetic acid and dithio acetic acid are respectively an aquo-thio acetic acid and a thio acetic acid. Thioacetamide,  $\text{CH}_3\text{CSNH}_2 \rightleftharpoons \text{CH}_3\text{C}(\text{NH})\text{SH}$ , is a thio-ammono acetic acid.

**Basic Nitrides and Acid Anammonides.** As the oxides of the more positive metals are frequently referred to as basic oxides so the nitrides of such metals may be called basic nitrides and as the oxides of the non-metals are known as acid oxides, or more generally as acid anhydrides, so we shall call the analogous non-metallic nitrides either acid nitrides or acid anammonides. Thus lithium nitride,  $\text{Li}_3\text{N}$ , calcium nitride,  $\text{Ca}_3\text{N}_2$ , and cuprous nitride,  $\text{Cu}_3\text{N}$ , for example, are basic nitrides, while carbonic nitride,  $\text{C}_3\text{N}_4$ , and phosphoric nitride,  $\text{P}_3\text{N}_5$ , chlorine nitride,  $\text{Cl}_3\text{N}$ , and acetonitrile,  $\text{CH}_3\text{CN}$ , are acid anammonides.

**Ammonobasic Salts and Aquobasic Salts.** Just as many salts are partially hydrolized by the action of water to form basic salts so analogous basic products are formed when certain salts are treated with liquid ammonia. The former as derivatives of water may be called aquobasic salts, the latter as derivatives of ammonia

are ammonobasic salts. Formulas for a number of basic salts are the following:



The first represents an ammonobasic mercuric chloride; the second, an aquobasic lead chloride; the third, an ammonobasic lead aquonitrate; the fourth, an aquobasic lead aquonitrate; the fifth, an ammonobasic calcium ammonocarbonate, and the sixth an aquobasic calcium ammonocarbonate. All these formulas excepting the fifth represent known compounds.

Many of the known mercury nitrogen compounds, among them the chloride of Millon's base,  $\text{HO-Hg-NH-Hg-Cl}$ , or  $\text{H}_2\text{N-Hg-O-Hg-Cl}$ , are to be regarded as salts which are basic at the same time to water and ammonia. They may be designated as aquobasic ammonobasic salts. (*Cf.* Chapter XII.)

**Acid Ammono Salts.** Two sodium salts of cyanamide of the formulas,  $\text{NaHNCN}$  and  $\text{Na}_2\text{NCN}$ , are known the first of which is an acid ammonocarbonate, the second a neutral or normal ammonocarbonate. Many salts of ammono and aquo-ammono acids are known which are acid salts. Sodium acetamidine,  $\text{CH}_3\text{C}(\text{NH})\text{-NHNa}$ , for example, is an acid sodium ammono-acetate, sodium acetamide,  $\text{CH}_3\text{CONHNa}$ , is an acid sodium aquo-ammono-acetate. It is interesting to note that these compounds may be looked upon, formally at least, as basic salts.

**Ammono Alcohols and Ammono Ethers.** The mono-alkylamines and the dialkylamines, since they are nitrogen analogs of the alcohols, are to be regarded as ammono alcohols, the trialkylamines as analogs of the ethers are ammono ethers. Methylamine and dimethylamine are ammono methyl alcohols. Trimethylamine is an ammono methyl ether.

**Ammono Esters.** Esters of ammono acids are known in large variety. Methylcyanamide,  $\text{CH}_3\text{NHCN}$ , dimethylcyanamide,  $(\text{CH}_3)_2\text{N-CN}$ , and triphenylguanidine,  $\text{C}_6\text{H}_5\text{N}=\text{C}(\text{NHC}_6\text{H}_5)_2$ , for example, are ammono carbonic acid esters, methylcarbylamine,  $\text{CH}_3\text{NC}$ , is a methyl ammonocarbonite, phenylbenzamidine,  $\text{C}_6\text{H}_5\text{C}(\text{NH})\text{NHC}_6\text{H}_5$ , *N-N'*-diphenylbenzamidine,  $\text{C}_6\text{H}_5\text{C}(\text{NC}_6\text{H}_5)\text{NHC}_6\text{H}_5$ , *N-N'*-diphenylbenzamidine,  $\text{C}_6\text{H}_5\text{C}(\text{NH})\text{N}(\text{C}_6\text{H}_5)_2$ , and triphenylbenzamidine,  $\text{C}_6\text{H}_5\text{C}(\text{NC}_6\text{H}_5)\text{N}(\text{C}_6\text{H}_5)_2$ , are phenyl ammonobenzoates, ethylchloramine,  $\text{C}_2\text{H}_5\text{NHCl}$ , diethylchloramine,  $(\text{C}_2\text{H}_5)_2\text{NCl}$ , and ethyldichloramine,  $\text{C}_2\text{H}_5\text{N}=\text{Cl}_2$ , are ethyl ammonohypochlorites. The formulas,  $\text{P}[\text{N}(\text{C}_2\text{H}_5)_2]_3$  and  $\text{Si}(\text{NHC}_2\text{H}_5)_4$ , represent respectively a hexaethyl ammonophosphite and a tetraethyl ammonosilicate. Three examples

of ester-salts are represented by the formulas,  $\text{CH}_3(\text{Ag})\text{NCN}$ ,  $\text{H}_2\text{C}(\text{NK})\text{N}(\text{C}_2\text{H}_5)_2$  and  $\text{CH}_3\text{C}(\text{NC}_6\text{H}_5)\text{NKC}_6\text{H}_5$ . The first compound is a silver methyl ammonocarbonate, the second a potassium diethyl ammonocarbonate, the third a potassium diphenyl ammonocarbonate.

**Aquo-Ammono Esters.** Alkyl and aryl derivatives of the aquo-ammono acids are to be regarded as aquo-ammono esters. The typical methylureas of the formulas,  $\text{CH}_3\text{O}-\text{C}(\text{NH})\text{NH}_2$  and  $\text{H}_2\text{N}-\text{C}(\text{NH})\text{NHCH}_3$ , are respectively an O-methyl and an N-methyl aquo-ammono-carbonate. The compound of the formula,  $\text{C}_6\text{H}_5\text{NH}-\text{C}(\text{NH})\text{NHK}$ , is a potassium phenyl aquo-ammono-carbonate. The formula  $\text{CH}_3\text{CO}-\text{N}(\text{Ti})\text{C}_6\text{H}_5$ , represents a compound which is at the same time a thallos salt and a phenyl ester of an aquo-ammono acetic acid.

**Ammono Aldehydes.** Accurately speaking nitrogen analogs of the aquo aldehydes are theoretically impossible. Approximate analogs of aquo benzaldehyde, for example, are benzyldeneimine  $\text{C}_6\text{H}_5\text{CH}=\text{NH}$ , benzyldenephenylimine,  $\text{C}_6\text{H}_5\text{CH}=\text{NC}_6\text{H}_5$ , and hydrazobenzamide,  $(\text{C}_6\text{H}_5\text{CH})_3\text{N}_2$ . We shall call the first compound an ammono benzaldehyde-alcohol, the second an ammono benzaldehyde ether, the third an ammono benzaldehyde-acetal.

**Carbazylic Acids.** The acid amidines are the nitrogen analogs of the carboxylic acids and as such might reasonably be called ammono carboxylic acids. It seems preferable however to adopt the designation given above. Three examples of carbazylic acids are formamidine,  $\text{HC}(\text{NH})\text{NH}_2$ , acetamidine,  $\text{CH}_3\text{C}(\text{NH})\text{NH}_2$ , and benzamidine,  $\text{C}_6\text{H}_5\text{C}(\text{NH})\text{NH}_2$ , which are respectively an ammono formic acid, an ammono acetic acid and an ammono benzoic acid.

**Carboxazylic Acids.** As has been explained above acetamide is to be looked upon as a mixed aquo-ammono acetic acid. Benzamide is an aquo-ammono benzoic acid. Oxamide is an aquo-ammono oxalic acid. The carboxylic acid amides constitute a group of compounds to which we shall frequently refer as carboxazylic acids. We may furthermore include the carboxylic acids, the carbazylic acids and the carboxazylic acids under the general designation of carbazylic acids.

**Ammonates, Ammonia of Crystallization.** A great many compounds are known which are related to ammonia as the ordinary hydrated salts, or salts containing water of crystallization, are related to water. Clearly such compounds may appropriately be called ammonates just as the analogous salt-water compounds are frequently called hydrates, or they may be referred to either as ammonated salts, or as salts with ammonia of crystallization. For example, the formula,  $\text{CaCl}_2 \cdot 8\text{NH}_3$ , represents a compound which may be described as calcium chloride containing eight molecules of an

monia of crystallization or it may be said to be octammonated calcium chloride.

**Ammonation, Deammonation.** When a basic oxide, an acid oxide or a salt takes up water the process involved is usually referred to as hydration. Inversely the loss of water from an aquo base, an aquo acid, a hydrated salt or even from a compound containing water in an indefinite state of combination is spoken of as dehydration. The analogous processes involving the taking up and losing ammonia may be conveniently designated as ammonation and deammonation respectively. When it becomes necessary to speak of ammonia-free salts in contradistinction to salts containing ammonia, whether adsorbed or as ammonia of crystallization, it will be convenient to speak of such ammonia-free products as deammonated salts or anammonous salts just as one speaks of dehydrated salts or anhydrous salts.

**Ammonolysis.** Many reactions are known to take place in liquid ammonia solution which are strictly analogous to the ordinary hydrolytic reactions brought about by the action of water. Such reactions may be suitably designated as ammonolytic, the processes involved as ammonolysis. Three examples of such ammonolytic reactions take place in accordance with the equations,  $\text{KNO}_3 + 2\text{NH}_3 = \text{KNN}_2 + 3\text{H}_2\text{O}$ ,  $\text{CH}_3\text{COOH} + 2\text{NH}_3 = \text{CH}_3\text{C}(\text{NH})\text{NH}_2 + 2\text{H}_2\text{O}$  and  $(\text{C}_2\text{H}_5)_2\text{NCN} + \text{NH}_3 = (\text{C}_2\text{H}_5)_2\text{NH} + \text{H}_2\text{N}^+\text{C}^-\text{N}$ , which represent the ammonolysis respectively of potassium aquonitrate to potassium ammononitrate (*cf.* Chapter XIV, p. 142) of acetic acid to its nitrogen analog known as acetamidine (*cf.* Chapter XXVIII, p. 262) and of a diethyl ammonocarbonate to an ammono carbonic acid and an ammono ethyl alcohol. (*Cf.* Chapter X, p. 97.)

**Nitridation.** Many metals when heated in an atmosphere of nitrogen are converted into nitrides. When sodium azide is added to fused sodium cyanide disodium cyanamide is formed. (*Cf.* Chapter XII, p. 130.) Methylamine when warmed in liquid ammonia solution with ammonium azide yields guanidine. (*Cf.* Chapter XXV, p. 229.) Iodine acts on benzylamine in liquid ammonia solution to form benzamidine. (*Cf.* Chapter XXV, p. 229.)

In view of the close analogy between these reactions and the oxidation of metals to metallic oxides, of sodium cyanide to sodium cyanate, of methyl alcohol to carbon dioxide and of benzyl alcohol to benzoic acid we of this laboratory have adopted the practise of speaking of nitridation when, as in the above examples, nitrogen plays a part analagous to that of oxygen in ordinary oxidation reactions. The reagents which bring about nitridation reactions may fittingly be called nitridizing agents.

**Augmentation (Augmention) and Reduction.** "In all chemistry there is no concept which is more fundamental than this one of

reduction and oxidation. Under the name of phlogistication and dephlogistication such processes were recognized even before the discovery of oxygen, and this mode of classifying phenomena has ever since been regarded as one of the greatest utility."<sup>2</sup>

In its earliest connotation oxidation meant simply union with oxygen while the inverse process of removing oxygen from an oxide was called reduction. These respective terms soon came to include processes involving the removal of hydrogen and union with hydrogen and finally to apply to a large variety of reactions in which oxygen and hydrogen take no part whatever. Thus for example when ferrous chloride is converted into ferric chloride by the action of chlorine the former salt is said to undergo oxidation to the latter while inversely the removal of chlorine from ferric chloride to form ferrous chloride or metallic iron, independently of the means whereby such removal is accomplished, is said to involve reduction; and when as products of the electrolysis of fused sodium chloride elementary chlorine and metallic sodium are formed at the anode and the cathode respectively it is said that oxidation takes place at the one electrode and reduction at the other. Using the term in the broad sense even nitrogen when it unites with metals to form metallic nitrides or with hydrogen to form ammonia may be said to function as an oxidizing agent.

Shifting our point of view for the moment from that of the oxygen chemist, so to speak, to that of the nitrogen chemist it appears at once that the term nitridation used in a broad sense becomes a synonym of oxidation. Our nitrogen chemist says that hydrogen undergoes nitridation when ammonia is formed by the interaction of nitrogen and hydrogen, that lithium when burned in an atmosphere of nitrogen is nitridized to lithium nitride and that metallic sodium and carbon are known to undergo nitridation to form disodium cyanamide when heated together in contact with nitrogen. Using the term in a broader sense he says that the conversion of a ferrous salt into a ferric salt involves nitridation be the transformation accomplished by nitric acid, hydrazoic acid, chlorine, oxygen or any other reagent effective to this end. He says furthermore that a nitridation reaction takes place when in liquid ammonia solution methylamine, an ammono methyl alcohol, is converted into cyanamide or guanidine by the action of hydrazoic acid or of iodine and that the action at the anode during electrolysis involves nitridation and this whether the electrolyte is in the fused state or in solution in water or in liquid ammonia. Finally, further generalizing the term, he says that the burning of lithium and of hydrogen in oxygen consists in the nitridation respectively of lithium to lithium oxide

<sup>2</sup> G. N. Lewis, "Valence and the Structure of Atoms and Molecules," *Am. Chem. Soc. Monograph*, New York, Chemical Catalog Co., Inc., 1923, p. 69.

and of hydrogen to water. It will be clear from these considerations that oxidation and nitridation become synonymous terms with the result that whether one speaks of oxidation or nitridation in the broad sense depends upon one's point of view.

Having added the word nitridation to our vocabulary we find ourselves seriously handicapped when attempts are made to discuss oxidation reactions using the term now in its specific sense and then in its broader meaning.

Emphasizing the confusion arising from the generalization of the term oxidation to include the many reactions in which oxygen takes no part, Cady and Taft<sup>3</sup> proposed the abandonment of oxidation and reduction as used in the broad sense and the substitution of deelectronation and electronation in their stead.<sup>4</sup>

The application of Cady and Taft's terminology to the electrolysis of fused sodium chloride, for example, is at once simple and clear. The action at the anode consists in the removal of an electron (deelectronation in the strict significance of the word) from the chlorine ion thereby forming a free chlorine atom which, uniting with a second deelectronized chlorine ion, escapes as elementary chlorine while the reducing action at the cathode consists in forcing the sodium ion to accept an electron with the result that metallic sodium is formed. The sodium ion is electronized.

So also the chloridation of ferrous chloride to ferric chloride and perhaps the oxidation of hydrogen to form water and the nitridation of hydrogen to ammonia may be said to involve electron transfers.

In other cases however, such for example as the oxidation of methyl alcohol to formaldehyde, formic acid and carbonic acid, complete transfer of electrons certainly does not take place.

In order to avoid the theoretical implications attaching to the terms electronation and deelectronation and the confusion arising from the use of oxidation and nitridation when understood in the broad sense we have chosen, for the purposes of this monograph, to use oxidation and nitridation each in its specific sense and to adopt the words augment and augmentation (augmentation) instead of oxidize and oxidation as used in the broad general sense. Augmentation is a reasonable antonym of reduction. The word is free from theoretical implications and is euphonically unobjectionable. The only burden laid upon the reader by our use of these terms will be

<sup>3</sup> Cady and Taft, *J. Phys. Chem.*, **29**, 1057 (1925); *Science*, **67**, 403 (1926).

<sup>4</sup> Cady and Taft's word deelectronation was modified to deelectron by Kirk and Browne [*J. Am. Chem. Soc.*, **50**, 337 (1928)]. With the above quotation from Lewis in mind and observing that at this late day the use of the words would carry no theoretical implications it would be reasonable and, were the words themselves not so awkward, perhaps desirable, to revive the terms phlogistication and dephlogistication.

to remember when he encounters the words augment and augmentation that they are used to mean oxidize and oxidation in the familiar general sense.

**Augmentation of Methane.** Assuming that all bonds between unlike atoms are more or less polarized it follows that methane may

$$\begin{array}{c} \text{H} \\ \vdots \\ \text{H} : \ddot{\text{C}} : \text{H} \\ \vdots \\ \text{H} \end{array}$$

be represented by the formula,  $\text{H} : \ddot{\text{C}} : \text{H}$ , in which the pairs of elec-

trons constituting the bonds are displaced toward the carbon atom and away from the hydrogen atoms as a result of the higher negativity of carbon as compared with hydrogen.<sup>5</sup>

It may be said that although shared by hydrogen the eight electrons are dominated by the carbon atom, that the carbon to hydrogen bond is somewhat polar and that therefore the carbon atom is in a reduced state in respect to the hydrogen atoms and that conversely the hydrogen atoms are in a corresponding state of augmentation.<sup>6</sup>

Since oxygen, nitrogen and chlorine, in the order named, are powerful electrophiles while the electron affinity of carbon is relatively weak it is reasonable to say when an hydroxyl group, an amino group or a chlorine atom takes the place of one of the hydrogen atoms in the methane molecule<sup>7</sup> that the electron pair constituting the bond is shifted away from the carbon to some unknown extent short of ionization<sup>8</sup> thereby augmenting the methane carbon atom to the states in which it exists in methyl alcohol, methylamine and methyl chloride respectively. The electron displacements thus assumed may be represented by the formulas,  $\text{H}_3\text{C}^+ : \text{H}$ ,  $\text{H}_3\text{C}^+ : \text{OH}$ ,

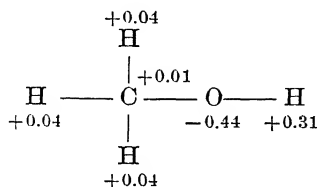
<sup>5</sup> Pauling [*J. Am. Chem. Soc.*, 54, 3577 (1932)] gives the following data, H = 0.00, P = 0.10, I = 0.40, S = 0.43, C = 0.55, Br = 0.75, Cl = 0.94, N = 0.95, O = 1.40, F = 2.00, for what he calls coordinates of the respective elements on the electronegativity scale.

<sup>6</sup> In a proper enough sense it may be said that the carbon atom in methane would be completely reduced (electronized) could ionization as represented by the equation,  $\text{CH}_4 \rightleftharpoons \text{C}^{--} + 4\text{H}^+$ , be assumed. It is reasonable to say that one of the carbon atom bonds in methylmagnesium iodide, if we may represent it by the formula,  $\text{CH}_3\text{Mg}^+\text{I}^-$ , is completely reduced, electronized at the expense of the magnesium atom, and that one of the bonds of the methane carbon atom is completely reduced in triphenylmethyl sodium,  $(\text{C}_6\text{H}_5)_3\text{C}^-\text{Na}^+$ , and, in so far as the one bond of the methyl carbon is concerned, augmented to the limit in triphenylmethyl chloride,  $(\text{C}_6\text{H}_5)_3\text{C}^+\text{Cl}^-$ . Both these compounds, it will be recalled, are electrolytes. [Wooster, *Chem. Rev.*, 11, 23 (1932).]

<sup>7</sup> Methane is very resistant to the action of oxidizing agents. None the less methyl alcohol has been identified among the products of its oxidation. Methylamine has not been obtained by the direct nitrification of methane. Methyl chloride is easily obtained by the action of chlorine on methane.

<sup>8</sup> With Pauling's electronegativity data in mind one would be inclined to say that the electron displacement is greatest in methyl alcohol, considerably less in methylamine and probably slightly less in methyl chloride than in methylamine.

$\text{H}_3\text{C}:\text{NH}_2$  and  $\text{H}_3\text{C}:\text{Cl}$ , the first formula indicating that in methane the carbon atom is negative in respect to hydrogen, the other three that it is positive when in combination with oxygen, nitrogen or chlorine. The extent to which these displacements take place is of course ignored here though Sidgwick<sup>9</sup> gives the formula,



to represent the residual charges between the constituent atoms in methyl alcohol.

In a similar manner methyl alcohol, methylamine and methyl chloride may be represented as undergoing augmentation, methyl alcohol, oxidation finally to carbon dioxide, methylamine, nitridation to an ammonio carbonic acid and methyl chloride, chloridation to carbon tetrachloride.

**Plus and Minus Signs.** Since the formulas,  $\text{CH}_3\cdot\text{-OH}$ ,  $\text{CH}_3\cdot\text{-NH}_2$  and  $\text{CH}_3\cdot\text{-Cl}$ , are quite the equivalents of the above provided one reads the small plus and minus signs \* as implying shifts of electron pairs together with concomitant polarity<sup>10</sup> and since moreover the use of such signs will be much more convenient than would be a scheme of representing polarity (augmentation-reduction) by means of colons placed nearer the negative atom of a more or less polar union compound we shall from time to time make use of the above and other similar formulas, examples of which are formaldehyde  $\text{H}_2\text{C}::\text{O}$ ,

formic acid  $\text{HC}::\begin{smallmatrix} \text{O} \\ \text{OH} \end{smallmatrix}$ , carbon dioxide  $\text{O}::\text{C}::\text{O}$ , dimethylamine  $\text{CH}_3\cdot\text{-NH}::\text{CH}_3$ , ethylideneimine  $\text{CH}_3\text{CH}::\text{NH}$ , formamidine  $\text{HC}::\begin{smallmatrix} \text{NH} \\ \text{NH}_2 \end{smallmatrix}$ , cyanamide  $\text{H}_2\text{N}::\text{C}::\text{N} \rightleftharpoons \text{HN}::\text{C}::\text{NH}$ , nitric acid  $\text{HO}::\text{N}::\begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix}$ , hydrazoic acid  $\text{HN}::\text{N}::\text{N}$ , nitrous acid,  $\text{HO}::\text{N}::\text{O}$ , triazene (ammonio ni-

<sup>9</sup> Sidgwick, "The Covalent Link in Chemistry," Cornell University Press, 1933, p. 156.

<sup>10</sup> Observing that Stieglitz first suggested that plus and minus signs be used to represent even the slightest displacement of the electron pair from the symmetrical position, Porter ["Molecular Rearrangements," American Chemical Society Monograph, New York, Chemical Catalog Co., Inc., 1928, p. 17] has made use of such formulas in his discussion of the molecular rearrangement of acetbromamide and similar compounds.

\* The small plus and minus signs printed here and elsewhere through the text are out of proportion. Either the minus signs should be smaller or the plus signs larger. The author and the publisher ask the indulgence of the reader as he reads these formulas.



trous acid)  $\text{H}_2\text{N} \cdot \text{N} \cdot \text{NH}$ , hypochlorous acid  $\text{HO} \cdot \text{Cl}$ , and chloramine  $\text{H}_2\text{N} \cdot \text{Cl}$ .

The small plus-minus signs will serve the purpose of representing polar covalent bonds<sup>11</sup> which is to say of indicating which of any two atoms held together by a covalent bond is augmented (oxidized, nitridized, deelectronized) with respect to the other and of telling something perhaps of such things as that methyl chloride, for example, reacts with potassium hydroxide to form methyl alcohol and potassium chloride and never by any chance to form methane and potassium hypochlorite or potassium methyl and hypochlorous acid.

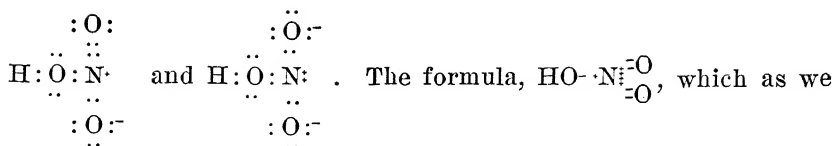
In our later discussions we shall from time to time use these plus minus signs to represent such distinctly polar unions as those which the strongly negative oxygen, nitrogen and chlorine and the strongly positive sodium, potassium and magnesium metals form with carbon, never for such bonds as those of carbon to carbon, and occasionally only to represent a hydrogen to carbon bond. The point that these signs are not to be read as representing complete electron transfers or ionization is especially emphasized. On occasion ionization bonds will be represented in the familiar manner with the plus and minus signs printed above and to the right of the respective ions,  $\text{Na}^+ \text{Cl}^-$ .

The colon and double colon will sometimes be used as in the formulas,  $\text{CH}_3 \cdot \text{N} \cdot \overset{\text{O}}{\underset{\text{O}}{\text{O}}}$  for nitromethane,  $\text{C}_6\text{H}_5 \cdot \text{N} \cdot \overset{\text{O}}{\underset{\text{O}}{\text{O}}} \cdot \text{C}_6\text{H}_5$ , for azoxybenzene,  $\text{H} \cdot \text{N} \cdot \overset{\text{O}}{\underset{\text{O}}{\text{O}}}$  for one of the tautomeric forms of nitrous acid,  $\text{C}_6\text{H}_5 \cdot \text{SO}_2\text{OH}$  for benzenesulfonic acid,  $\text{H}_2\text{N} \cdot \text{NH}_2$  for hydrazine,  $\text{HN} \cdot \text{N}$  for an unknown diimide (azo compounds),  $\overset{\text{HN}}{\underset{\text{N}}{\text{N}}} \cdot \text{N}$  and  $\text{HN} \cdot \overset{\text{N}}{\underset{\text{N}}{\text{N}}}$  for hydrazoic acid regarded respectively as a cyclic nitrous acid hydrazide and as an ammono hyponitrous acid, and  $\text{H}_2\text{N} \cdot \text{OH}$  or  $\text{H}_3\text{N} \cdot \text{O}$  for hydroxylamine, to represent nonpolar bonds or bonds concerning the polarity of which no opinion is expressed.

Objections to some of the above formulas may be raised and especially, for example, to those written for nitric acid and its derivatives in that these compounds are represented as containing pentavalent nitrogen. However, even assuming the impossibility of pentacovalent nitrogen, it may still be maintained that the nitrogen atom in nitric acid is, in a proper enough sense, pentapositive valent.

Two formulas which have been assigned to nitric acid are,

<sup>11</sup> W. A. Noyes [*Z. physik. Chem.*, 130, 329 (1927)] calls such bonds potentially polar.



shall endeavor to show differs in no essential respect from the preceding two, has been adopted for occasional use in this monograph.

The first formula represents the nitrogen atom in nitric acid as pentavalent provided one defines the valence of nitrogen as the arithmetical sum of its four covalences<sup>12</sup> and the one bond represented by the plus and minus signs. Or stated in another way the pentavalence of the nitrogen atom is made up of three covalences and one of Sidgwick's<sup>13</sup> coordinate covalences or Lowry's semipolar double bond. In still other words it may be said that the nitrogen atom in this formula is tetravalent unelectrovalent. The second formula, which may perhaps be regarded as differing from the first in no essential way, represents the nitrogen atom as tricovalent dielectrovalent.

Assuming now that the mean positions of the electron pairs shared by the nitrogen atom with the oxygen atoms are displaced or in some wise constrained toward the highly negative oxygen atoms and away from the nitrogen atom we arrive at a picture of the nitric acid molecule represented by the third formula above in which all three oxygen atoms are indicated as more or less negative in respect to the nitrogen atom. The nitrogen atom in nitric acid is pentapositive, in a reasonable enough sense pentapositive valent. In the language of W. A. Noyes, already referred to (p. 14) the nitrogen atom is potentially pentapositive, the oxygen atoms potentially dinegative.

Of the several formulas for hydrazoic acid which have been proposed on the assumption that the acid is a straight chain compound,  $\text{H}:\ddot{\text{N}}::\ddot{\text{N}}::\ddot{\text{N}}\cdot$ , seems most satisfactory. In this formula the middle nitrogen atom is represented as tetravalent unipositive, the right-hand atom as dicovalent uninegative, the left-hand one either as tricovalent or as dicovalent uninegative depending upon whether one considers the hydrogen atom as covalently attached to the nitrogen atom or to exist as an ion.

With the above discussion of the formulas for nitric acid in mind it will be clear that the formula,  $\text{HN}::\text{N}::\text{N}$ , for hydrazoic acid differs in no fundamental way from the preceding one provided that it be assumed that the middle nitrogen atom is pentapositive in re-

<sup>12</sup> According to Langmuir [*J. Am. Chem. Soc.*, **41**, 926 (1919)] covalence denotes the number of pairs of electrons which an atom shares with its neighbors.

<sup>13</sup> Sidgwick, "The Electron Theory of Valence," Cornell University Press, 1927, p. 60.

spect to the other two and that of the three plus-minus signs at the right-hand end of the formula two be read as representing polarized covalent bonds and that the third bond, call it what we may, results from the contribution on the part of the middle nitrogen atom of three of the four electrons constituting the dicovalent linkage.

It is reasonable enough to say that the nitrogen atom in nitric acid is pentapositive as a result of the powerful electron affinity of oxygen in displacing the shared electrons away from the nitrogen atom and into the nearer neighborhood of the oxygen atoms. Why however the middle nitrogen atom in hydrazoic acid should be pentapositive is not clear. Even so, very definite justification for the view that such is the case appears when the experimental fact is recalled that potassium azide is formed by the ammonolysis of potassium nitrate. (*Cf.* Chapter XIV, p. 142.) Representing the reaction

involved by the equation,  $\text{KO} \cdot \text{N} \begin{smallmatrix} \text{=O} \\ \text{=O} \end{smallmatrix} + 2\text{NH}_3 = \text{KN} \text{= :N:} \text{=N} + 3\text{H}_2\text{O}$ ,

it would seem to follow that the nitric acid nitrogen present in potassium nitrate persists as such in its ammonolytic product.

Two important papers upon the constitution of hydrazoic acid have been published since this chapter was written.

Considerations similar to those used in the discussion of nitric acid may be taken to justify our proposed use of the respective formulas,  $\text{HO} \cdot \text{N} \text{=O}$ ,  $\text{HO} \cdot \text{N} \text{:} \text{=NH} \rightleftharpoons \text{O} \text{:} \text{N} \cdot \text{NH}_2$  and  $\text{H}_2\text{N} \cdot \text{N} \text{:} \text{=NH}$ , for aquo nitrous acid, an aquo-ammono nitrous acid and an ammono nitrous acid.

Finally we bring this chapter on nomenclature to a close by stating that in the succeeding chapters we shall for the most part make use of the classical formulas of the organic chemist introducing plus and minus signs, colons and double colons only when it is deemed that clarity in the discussion of certain reactions will be thereby enhanced.

## CHAPTER V.

### AUGMENTATION AND REDUCTION IN LIQUID AMMONIA.

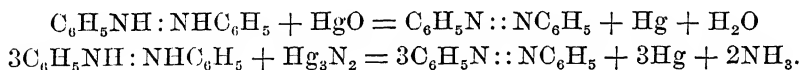
In this chapter are given examples of augmentation and reduction reactions which have been observed to take place in liquid ammonia solution.

**Nitridizing Agents.** Hydrazoic acid, iodamine<sup>1</sup> and certain heavy metal amides, imides and nitrides have been observed to enter into reactions in a manner closely resembling those which take place when their respective oxygen analogs, nitric acid, hypiodous acid and the heavy metal hydroxides and oxides act as oxidizing agents. The following examples will bring out clearly the striking resemblances between the action of the former compounds, which we propose to designate as nitridizing agents, and the oxidizing action of the more familiar oxidizing agents.

1. The nitridizing action of hydrazoic acid is discussed in some detail in later chapters. (*Cf.* Chapters XIV and XXV.)

2. Hydrazobenzene is converted into azobenzene, in water by the action of mercuric oxide, in liquid ammonia by the action of mercuric nitride.<sup>2</sup>

The reactions in the respective solvents take place in accordance with the equations,



The water chemist, so to speak, would be inclined to read the first equation as representing the oxidation, the ammonia chemist to read the second equation as representing the nitridation of hydrazobenzene to azobenzene even in face of the fact that neither in the one case does the oxygen of the mercuric oxide nor in the other the nitrogen of the mercuric nitride have anything to do with the reactions involved. It would be better to say that dipositive mercury in undergoing reduction augments (deelectronizes) the hydrazine nitrogen to azo nitrogen. It is clear that the hydrazo group in pass-

<sup>1</sup> Arbitrarily assumed to be present in liquid ammonia solutions of iodine.

<sup>2</sup> Schurman and Fernelius, *J. Am. Chem. Soc.*, 52, 2425 (1930). Fernelius reports (private communication) that cuprous nitride, silver amide, thallous nitride, bismuth nitride, lead imide and sulfur nitride bring about the augmentation of hydrazobenzene to azobenzene.

ing to the azo group loses two electrons along with the two hydrogen atoms.

3. By the augmenting action of iodine hydrazobenzene, in liquid ammonia solution, is dehydrogenated as represented by the equation,  $C_6H_5NH:NHC_6H_5 + 2I = C_6H_5N::NC_6H_5 + 2HI$ , to form azobenzene.<sup>3</sup>

4. Bergstrom<sup>4</sup> found that potassium ammonostannite is nitridized to potassium ammonostannate when, in liquid ammonia solution in the presence of potassium amide, it is subjected to the action of iodine. The reactions involved take place as represented by the equation,  $SnNK + 2I + 3KNH_2 = Sn(NK)_2 + 2KI + 2NH_3$ . Clearly stannous tin is augmented to stannic tin while concomitantly iodine is reduced to hydriodic acid iodine.

**Electrolytic Nitridation.** 1. In a paper entitled "The Electrolytic Nitridation of Various Anodes in a Solution of Ammonium Trinitride," Browne, Holmes and King<sup>5</sup> give an account of the electrolytic action of liquid ammonia solutions of hydrazoic acid on anodes of copper, silver, cadmium, aluminum, lead, antimony, iron and nickel. Although none of the electrolytic products was analyzed quantitatively it was nevertheless definitely shown that, excepting in the case of aluminum, the respective metallic azides were formed by the deelectronizing action at the anode.

2. Turrentine and Moore<sup>6</sup> found that metallic azides are formed when a water solution of sodium azide is electrolyzed using metallic anodes and said that the action at the anode consists in the nitridation of the metals to their respective trinitrides. The reaction at a silver anode for example, consists simply in the deelectronation of metallic silver to silver ions which in the presence of azide ions separate from solution as insoluble silver azide.

3. Cady and Taft<sup>7</sup> report that metallic thallium is deposited on the cathode and that thallic iodide appears in solution when a liquid ammonia solution of thalious iodide is subjected to electrolysis between platinum electrodes and that azobenzene is formed when electricity is passed through a liquid ammonia solution containing hydrazobenzene. Unipositive thallium is augmented to tripositive thallium at the anode and reduced to the metallic state at the cathode. Hydrazobenzene is dehydrogenated to azobenzene by the augmenting action at the anode.

4. Fulton and Bergstrom<sup>8</sup> have shown that just as carbon diox-

<sup>3</sup> Schurman and Fernelius, *J. Am. Chem. Soc.*, **52**, 2425 (1930).

<sup>4</sup> Bergstrom, *J. Am. Chem. Soc.*, **32**, 440 (1928).

<sup>5</sup> Browne, Holmes and King, *J. Am. Chem. Soc.*, **41**, 1769 (1919).

<sup>6</sup> Turrentine and Moore, *J. Am. Chem. Soc.*, **34**, 375 (1912); Turrentine, *J. Am. Chem. Soc.*, **33**, 803 (1911).

<sup>7</sup> Cady and Taft, *J. Phys. Chem.*, **29**, 1070 (1928).

<sup>8</sup> Fulton and Bergstrom, *J. Am. Chem. Soc.*, **56**, 167 (1934).

ide and ethane are formed at the anode during the electrolysis of potassium acetate in water solution, so the electrolysis of potassium acetamidine (potassium ammonioacetate) in liquid ammonia solution yields cyanamide, which is an ammonio carbonic acid, and ethane among the anode products. In the one case the deelectronized aquo-acetate ion yields ethane and carbon dioxide,  $2\text{CH}_3\text{COO} = \text{CH}_3\text{CH}_3 + 2\text{CO}_2$ , in the other the deelectronized ammonioacetate ion breaks down to form ethane and cyanamide,  $2\text{CH}_3\text{C}(\text{NH})\text{NH} = \text{CH}_3\text{CH}_3 + 2\text{H}_2\text{NCN}$ .

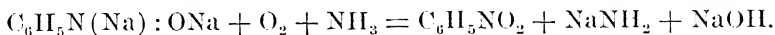
**Oxidation in Liquid Ammonia Solution.** 1. Kraus and Whyte<sup>9</sup> showed that an equimolecular mixture of potassium hydroxide and potassium amide is formed when a slow current of oxygen is passed into a cold solution of metallic potassium in liquid ammonia. The reactions involved take place as represented by the empirical scheme,  $2\text{K} \xrightarrow{+\text{O}} \text{K}_2\text{O} \xrightarrow{+\text{NH}_3} \text{KOH} + \text{KNH}_2$ , in accordance with which the potassium oxide formed by the oxidation of metallic potassium undergoes ammonolysis to yield potassium hydroxide and potassium amide. Sodium, cesium and rubidium undergo oxidation in much the same manner.

2. Kraus and Whyte found furthermore that potassium amide is oxidized to potassium nitrite,  $\text{KNH}_2 + 3\text{O} = \text{KNO}_2 + \text{H}_2\text{O}$ , when oxygen is bubbled through a liquid ammonia solution of the ammonio base. The water formed reacts with potassium amide with the result that in accordance with the equation,  $2\text{KNH}_2 + 3\text{O} = \text{KNO}_2 + \text{KOH} + \text{NH}_3$ , one molecule each of potassium nitrite, potassium hydroxide and ammonia are obtained for each two molecules of potassium amide used.

3. Rengade<sup>10</sup> found that cesium amide under similar treatment yields cesium nitrite and cesium hydroxide together with a small amount of cesium nitrate.

Sodium amide reacts with oxygen in much the same manner on exposure to the atmosphere.<sup>11</sup>

4. White and Knight<sup>12</sup> found that nitrobenzene is formed when a current of air is passed through a liquid ammonia solution of disodium phenylhydroxylamine. It appears that phenylhydroxylamine is thereby oxidized to nitrobenzene as represented empirically by the equation,



<sup>9</sup> Kraus and Whyte, *J. Am. Chem. Soc.*, **48**, 1781 (1926); Joannis, *Compt. rend.*, **110**, 1370 (1893).

<sup>10</sup> Rengade, *Ann. chim. phys.*, [8] 348 (1907).

<sup>11</sup> Schrader, *Z. anorg. Chem.*, **108**, 44 (1919).

<sup>12</sup> White and Knight, *J. Am. Chem. Soc.*, **45**, 1785 (1923).

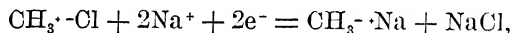
**Reducing Action of the Alkali Metals in Liquid Ammonia Solution.** A few examples of the reducing action of metallic sodium in liquid ammonia solution are the following.

1. When silver iodide and metallic sodium are brought together in liquid ammonia solution metallic silver is precipitated while sodium iodide remains in solution. As represented by the equation,  $\text{AgI} + \text{Na} = \text{Ag} + \text{NaI}$ , the reaction consists in the augmentation of metallic sodium to sodium ions and the reduction of silver ions to metallic silver.<sup>13</sup>

It will be recalled that Kraus<sup>14</sup> has shown that the alkali and alkaline earth metals exist in liquid ammonia solutions in the form of metallic ions and ammoniated electrons, which is to say that by the simple act of going into solution metallic sodium is augmented to sodium ions. This being the case the silver iodide silver ion is reduced by simply combining with a free electron,  $\text{Ag}^+ + e^- = \text{Ag}$ .

2. By the interaction of zinc cyanide and metallic sodium in liquid ammonia solution sodium cyanide and an insoluble zinc sodium compound (sodium zincide) are formed in the proportions represented by the equation,  $4\text{Zn}(\text{CN})_2 + 9\text{Na} = \text{NaZn}_4 + 8\text{NaCN}$ .<sup>15</sup> Two reactions are undoubtedly involved, the first consisting in the formation of sodium cyanide and metallic zinc,  $\text{Zn}(\text{CN})_2 + 2\text{Na} = 2\text{NaCN} + \text{Zn}$ , the second in the formation of a sodium zinc compound  $\text{Na} + 4\text{Zn} = \text{NaZn}_4$ , which separates from solution as a practically insoluble precipitate.

3. Chablay<sup>16</sup> has shown that methyl chloride is reduced to methane when passed into a liquid ammonia solution of metallic sodium and that at the same time methylamine is formed. The reducing action involved may be represented by the equation,



in accordance with which the free electrons present in the sodium solution reduces the methyl carbon from the state in which it exists in methyl chloride to that in which it is present in sodium methyl.<sup>17</sup> The sodium methyl thus formed is immediately ammonolyzed in the presence of liquid ammonia to methane and sodium amide,  $\text{CH}_3\text{Na} + \text{NH}_3 = \text{CH}_4 + \text{NaNH}_2$ . The methylamine is formed as a product of the interaction of methyl chloride and sodium amide,  $\text{CH}_3\text{Cl} + \text{NaNH}_2 = \text{CH}_3\text{NH}_2 + \text{NaCl}$ .

<sup>13</sup> Burgess and Smoker, *J. Am. Chem. Soc.*, **52**, 3573 (1930).

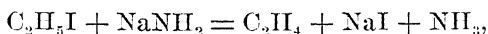
<sup>14</sup> Kraus, *J. Am. Chem. Soc.*, **44**, 1216 (1922).

<sup>15</sup> Burgess and Ross, *J. Am. Chem. Soc.*, **51**, 2127 (1929).

<sup>16</sup> Chablay, *Ann. chim.*, [9] **1**, 469 (1914); see also Lebeau, *Compt. rend.*, **140**, 1040 (1905).

<sup>17</sup> Franklin [*J. Am. Chem. Soc.*, **46**, 2137 (1924)] has suggested that sodium methyl may be regarded as a base of a methane system.

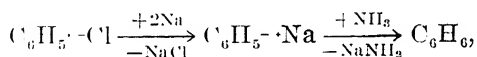
Other alkyl halides are acted upon by metallic sodium in a similar manner excepting that in addition to the saturated hydrocarbons and amines considerable yields of unsaturated hydrocarbons are obtained. Thus, for example, when Chablay added ethyl iodide to a liquid ammonia solution of sodium yields of 75 per cent ethane, four per cent of ethylene together with an undetermined amount of ethylamine were obtained. The reactions involved are similar to those formulated above excepting that a portion of the ethyl iodide reacts with sodium amide,



to form ethylene, sodium iodide and ammonia. It will be recalled that sodium hydroxide acts on ethyl iodide to form ethylene, sodium iodide and water.

4. By the action of metallic sodium in liquid ammonia solution Chablay<sup>18</sup> accomplished the reduction of a number of acid amides and carboxylic acid esters to aquo alcohols. For example acetamide was reduced to ethyl alcohol and methyl butyrate to butyl alcohol.

5. White<sup>19</sup> found that benzene, aniline, diphenylamine and triphenylamine are formed when phenyl chloride is added to an excess of metallic sodium in liquid ammonia solution. The reduction of phenyl chloride to benzene presumably takes place as represented by the scheme,



in accordance with which phenyl sodium, resulting from the interaction of phenyl chloride and metallic sodium, undergoes ammonolysis to form benzene and sodium amide. The other three compounds are probably formed by the interaction of sodium amide and phenyl chloride as represented by the equations,

- (1)  $\text{C}_6\text{H}_5\text{Cl} + \text{NaNH}_2 = \text{C}_6\text{H}_5\text{NH}_2 + \text{NaCl},$
- (2)  $\text{C}_6\text{H}_5\text{NHNa} + \text{C}_6\text{H}_5\text{Cl} = \text{C}_6\text{H}_5\text{NHC}_6\text{H}_5 + \text{NaCl},$
- (3)  $(\text{C}_6\text{H}_5)_2\text{NNa} + \text{C}_6\text{H}_5\text{Cl} = (\text{C}_6\text{H}_5)_3\text{NC}_6\text{H}_5 + \text{NaCl}.$

It is known that  $\text{C}_6\text{H}_5\text{NHNa}$  is formed by the action of sodium on aniline,  $(\text{C}_6\text{H}_5)_2\text{NK}$  by the action of potassium on diphenylamine.

6. Kraus and Kawamura<sup>20</sup> found that sodium chloride and the

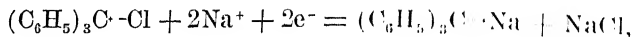
<sup>18</sup> Chablay, *Ann. chim.*, [9] **8**, 201 (1917).

<sup>19</sup> White, *J. Am. Chem. Soc.*, **45**, 779 (1925).

<sup>20</sup> Kraus and Kawamura, *J. Am. Chem. Soc.*, **45**, 2756 (1923); see also Kraus and Rosen, *J. Am. Chem. Soc.*, **47**, 2739 (1925).



sodium salt of triphenylmethyl are formed when triphenylmethyl chloride and metallic sodium are brought together in liquid ammonia solution. The reactions involved may be represented by the equation,



and explained as consisting in the reduction of the triphenylmethyl carbon from the state in which it exists in triphenylmethyl chloride to that in which it is present in triphenylmethyl sodium. In solution in liquid ammonia triphenylmethyl sodium and triphenylmethyl chloride are good conductors of electricity. Triphenylmethane is a very poor conductor.

7. By the action of sodium in liquid ammonia solution White and Knight<sup>21</sup> accomplished the reduction of nitrobenzene and of nitrosobenzene to phenylhydrazine, of azoxybenzene to azobenzene, of azobenzene to hydrazobenzene and of hydrazobenzene to aniline.

8. On the basis of the reducing action of metallic sodium in liquid ammonia solution an excellent procedure for the quantitative determination of the halogens in organic compounds has been developed.<sup>22</sup>

Further examples of augmentation and reduction reactions taking place in liquid ammonia will be encountered as we proceed.

<sup>21</sup> White and Knight, *J. Am. Chem. Soc.*, **45**, 1786 (1923).

<sup>22</sup> Chablay, *Ann. chim.*, [9] **1**, 510 (1914); Clifford, *J. Am. Chem. Soc.*, **41**, 1051 (1919); Dains and Brewster, *J. Am. Chem. Soc.*, **42**, 1573 (1920).

## CHAPTER VI.

### AMMONO BASES AND BASIC NITRIDES.

The metallic amides and imides are bases of the nitrogen system. The metallic nitrides are the analogs of the basic oxides.

Just as water acts on the alkali and alkaline earth metals to form metallic hydroxides so, excepting that the speeds of the reactions are incomparably slower, liquid ammonia acts on the same metals to yield the analogous metallic amides. The amides of potassium, rubidium and cesium are abundantly soluble in liquid ammonia, sodium amide is somewhat soluble, lithium amide and the alkaline earth amides are all but insoluble while other metallic amides and imides are quite insoluble.

Insoluble metallic amides, imides and nitrides have been obtained by adding potassium amide in solution in liquid ammonia to liquid ammonia solutions of metallic salts, just as in water solutions many metallic hydroxides and oxides are precipitated by the action of potassium hydroxide on soluble metallic salts. With the exception of the noble metals practically all known metals are reported to form nitrides.

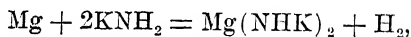
**Potassium Amide,  $\text{KNH}_2$ .** This typical ammono base, a caustic potash of the nitrogen system and one of the two theoretically possible nitrogen analogs of potassium hydroxide, potassium imide being unknown, was first prepared many years ago by Gay Lussac and Thénard<sup>1</sup> by heating metallic potassium in an atmosphere of ammonia.

When metallic potassium is brought into contact with liquid ammonia, instead of reacting vigorously with the liquid as it does with water, it quietly dissolves to form an intensely blue solution from which the metal may be recovered by evaporating away the solvent. The metal in solution reacts with the pure solvent at a rate which is extremely slow. At ordinary temperatures the conversion of a few centigrams of metallic potassium in solution in liquid ammonia into the metallic amide takes days or even months. The action of the solvent on the metal is somewhat accelerated by sunlight and also by the presence of certain salts in solution. Many metals actively catalyze the reaction between the solvent and the metal in

<sup>1</sup> Gay Lussac and Thénard, *Recher. physicochim.*, **1**, 337, Paris (1811); cf. H. Davy, *Phil. Trans.*, **99**, 40, 450 (1809).

solution.<sup>2</sup> A relatively minute amount of platinum black, for example, or a spiral of iron wire, placed in a liquid ammonia solution of metallic potassium causes an immediate and fairly vigorous evolution of hydrogen gas with the result that a considerable quantity of the metal is converted into the amide in the course of a few minutes. The preparations of potassium amide used in the experiments described in this and subsequent chapters of this monograph were obtained in this manner.

Potassium amide melts at 329°.<sup>3</sup> It dissolves rapidly and abundantly in liquid ammonia to form a solution from which, when sufficiently concentrated, it separates in the form of colorless leaflets without ammonia of crystallization. The crystals deliquesce in contact with ammonia vapor of such a concentration as to be in equilibrium with liquid ammonia at laboratory temperatures. A saturated solution at -33° contains about 45 grams of the base in 100 cc. of solution.<sup>4</sup> In the fused state and in solution in liquid ammonia potassium amide is a good conductor of electricity. It neutralizes acids in solution in liquid ammonia to form salts, saponifies esters, precipitates metallic amides, imides and nitrides from solutions of salts of heavy metals. In the fused state and also in solution in liquid ammonia it attacks certain metals, metallic magnesium, for example, in accordance with the equation,



to form potassium ammonomagnesiate. (See Chapter VII.) Clearly the resemblance between potassium amide and potassium hydroxide is a striking one.

Potassium amide is vigorously hydrolyzed by the action of water,  $\text{KNH}_2 + \text{H}_2\text{O} = \text{KOH} + \text{NH}_3$ , and is rapidly oxidized on exposure to the atmosphere as represented by the equation,  $2\text{KNH}_2 + 3\text{O}_2 = 2\text{KNO}_2 + 2\text{H}_2\text{O}$ .<sup>5</sup>

**Sodium Amide,  $\text{NaNH}_2$ .** This sodium ammono base was first prepared by Gay Lussac and Thénard by the action of ammonia gas on melted sodium heated to a temperature of about 300°. It may be obtained quite colorless and in a high state of purity by dissolving metallic sodium in liquid ammonia and then placing in the solution a spiral of iron wire which catalytically accelerates the otherwise very slow reaction,  $\text{Na} + \text{NH}_3 = \text{NaNH}_2 + \text{H}_2$ , which takes place between the metal and the solvent. The slightly soluble

<sup>2</sup> Franklin, *J. Am. Chem. Soc.*, 27, 830 (1905).

<sup>3</sup> Kraus and Cuy, *J. Am. Chem. Soc.*, 45, 712 (1923).

<sup>4</sup> Franklin, *Z. physik. Chem.*, 69, 290 (1909).

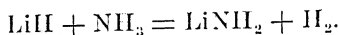
<sup>5</sup> Schrader, *Z. anorg. Chem.*, 108, 44 (1919); see also Kraus and Whyte, *J. Am. Chem. Soc.*, 48, 1781 (1926).

amide separates from the solution well crystallized. It is also obtained as a crystalline precipitate by adding a liquid ammonia solution of potassium amide to a similar solution of sodium iodide,  $\text{KNH}_2 + \text{NaI} = \text{NaNH}_2 + \text{KI}$ , and by the action of potassium amide on an excess of metallic sodium in solution in liquid ammonia in accordance with the equation,  $\text{KNH}_2 + \text{Na} = \text{NaNH}_2 + \text{K}$ .

Sodium amide melts at  $206.4^\circ$ . It is soluble in liquid ammonia to the extent of 1.5 gram per liter at  $20^\circ$ . It is energetically hydrolyzed in the presence of water to sodium hydroxide and ammonia. When heated to temperatures around  $350^\circ$  it decomposes into metallic sodium, ammonia, nitrogen and hydrogen. Both in the fused state and in solution in liquid ammonia it is a conductor of electricity.

Fused sodium amide dissolves metallic magnesium, zinc, molybdenum and tungsten, quartz, glass, many natural silicates and a wide variety of other compounds.<sup>7</sup> Neither an imide nor a nitride of sodium is known.

**Lithium Amide,  $\text{LiNH}_2$ , Lithium Imide,  $\text{Li}_2\text{NH}$  and Lithium Nitride,  $\text{Li}_3\text{N}$ .** Lithium amide<sup>8</sup> has been obtained, (1) by heating metallic lithium in a current of ammonia gas, (2) by the action of liquid ammonia on lithium in the presence of platinum black acting as a catalyst, (3) by adding potassium amide to a liquid ammonia solution of metallic lithium,  $\text{Li} + \text{KNH}_2 = \text{LiNH}_2 + \text{K}$ , or of lithium iodide,  $\text{LiI} + \text{KNH}_2 = \text{LiNH}_2 + \text{KI}$ , (4) by the ammonation of lithium nitride,  $\text{Li}_3\text{N} + 2\text{NH}_3 = 3\text{LiNH}_2$ , and (5) by warming lithium hydride in an atmosphere of ammonia,



When prepared by reactions carried out in liquid ammonia solution lithium amide is obtained as a colorless, crystalline powder which melts at  $373^\circ$  to  $375^\circ$ . It is practically insoluble in liquid ammonia. When heated to  $360^\circ$  to  $450^\circ$ , according to Ruff and Georges,  $620^\circ$  to  $640^\circ$  according to Dafert and Miklausz, lithium amide is converted into lithium imide. Lithium imide apparently has not been deammonated to the nitride.

Lithium nitride is formed when metallic lithium is gently heated in an atmosphere of nitrogen.<sup>9</sup> Even at laboratory temperature, according to Deslandres, nitrogen is absorbed by metallic lithium.<sup>10</sup>

<sup>6</sup> Kraus and Cuy, *J. Am. Chem. Soc.*, **45**, 712 (1923).

<sup>7</sup> Bergstrom and Fernelius, *Chem. Rev.*, **12**, 67 (1933).

<sup>8</sup> Titherley, *J. Chem. Soc.*, **65**, 504 (1894); **71**, 469 (1897); Ruff and Geisel, *Ber.*, **39**, 842 (1906); Ruff and Georges, *Ber.*, **44**, 504 (1911); Dafert and Miklausz, *Monatsh.*, **31**, 981 (1910); **33**, 63 (1912); Franklin, *J. Phys. Chem.*, **23**, 49 (1919).

<sup>9</sup> Deslandres, *Compt. rend.*, **121**, 886 (1895).

<sup>10</sup> Guntz, *Compt. rend.*, **123**, 995 (1896).

According to Dafert and Miklauz, lithium nitride melts at  $840^{\circ}$  to  $845^{\circ}$  and at  $870^{\circ}$  rapidly attacks iron, nickel, copper, platinum, magnesia, porcelain and other silicates.

Rubidium Amide,  $\text{RbNH}_2$ , and Cesium Amide,  $\text{CsNH}_2$ . Both these amides have been formed from the respective metals<sup>11</sup> following procedures already described in connection with the discussion of the amides of potassium and sodium.

Ammonous Cuprous Nitride,  $\text{Cu}_3\text{N} \cdot x\text{NH}_3$  and Cuprous Nitride,  $\text{Cu}_3\text{N}$ .<sup>12</sup> The bulky, amorphous precipitates formed by the action of potassium hydroxide on solutions of heavy metal salts, generally looked upon as metallic hydroxides, are illuminatingly discussed by Weiser as hydrous oxides.<sup>13</sup>

Just as many of these hydrous oxides when subjected to drying processes lose water continuously without forming definite compounds short of the metallic oxides, so certain likewise bulky, amorphous precipitates formed by the action of potassium amide on metal salts in liquid ammonia solution show an entirely similar behavior. From considerations of analogy such products may be called ammonous nitrides.

When potassium amide is added to a liquid ammonia solution of cupric nitrate a dark green precipitate is formed and at the same time nitrogen is set free in the ratio of one atom of nitrogen to three molecules of cupric nitrate used.

On standing for some time in contact with the supernatant solution the color of the precipitate changes to brick red. Dried, that is to say freed from ammonia, in vacuum at laboratory temperature the precipitate takes on a dark brown color and has then roughly the composition of cuprous imide. When a high vacuum is maintained over this precipitate slow evolution of ammonia continues for a long time but apparently ceases short of the formation of cuprous nitride. At  $160^{\circ}$  cuprous nitride is formed.

The following observations show that pure ammonous cuprous nitride is a colorless substance and that the color of the products described above is due to the presence of small admixture of cupric copper.

When the colored precipitate formed by adding potassium amide to a solution of cupric nitrate is dissolved in ammonium nitrate, that is to say in a liquid ammonia solution of nitric acid, the pale blue color of the solution obtained shows the presence of small amounts of cupric copper. When on the other hand

<sup>11</sup> Titherley, *J. Chem. Soc.*, **71**, 469 (1897); Moissan, *Compt. rend.*, **136**, 587, 1177 (1903); Ruff and Geisel, *Ber.*, **39**, 828 (1906); Franklin, *J. Phys. Chem.*, **23**, 46 (1919).

<sup>12</sup> Fitzgerald, *J. Am. Chem. Soc.*, **29**, 657 (1907); Franklin, *J. Am. Chem. Soc.*, **34**, 1501 (1912); Warren, *Chem. News*, **55**, 155 (1887).

<sup>13</sup> Weiser, "The Hydrous Oxides," New York, McGraw-Hill Book Co., Inc., 1926, p. 192.

the colored precipitate is dissolved in potassium amide an entirely colorless solution of potassium ammonocuprite (*cf.* Chapter VII, p. 70) is formed. Addition of ammonium nitrate to this solution precipitates pure white ammonous cuprous nitride. Further addition of nitric acid dissolves this precipitate to form a colorless solution of cuprous nitrate from which pure white ammonous cuprous nitride is again precipitated by adding potassium amide. The colorless solution of cuprous nitrate on standing, especially in sunlight, gradually takes on a pale blue color indicative of the slow formation of cupric copper. On adding potassium amide to this pale blue solution the original colored precipitate appears. The three-legged reaction tube in Figure 4 (p. 33) was used in making these observations.

This formation of a small amount of cupric salt when cuprous nitrate solution is allowed to stand is in harmony with the observations of Sloan,<sup>14</sup> who, in preparing cuprous nitrate by the reducing action of metallic copper on cupric nitrate in liquid ammonia solution, was unable to discharge entirely the blue color of his solutions.

Cuprous nitride explodes with considerable violence at a temperature around 240°. By the action of dilute aqueous sulfuric acid it is converted into equivalent quantities of cupric sulfate and metallic copper.

**Silver Amide,  $\text{AgNH}_2$ .** A pure white, amorphous and rather bulky precipitate of silver amide is formed in accordance with the equation,  $\text{AgNO}_3 + \text{KNH}_2 = \text{AgNH}_2 + \text{KNO}_3$ , when a solution of potassium amide is run into a liquid ammonia solution of a soluble silver salt.<sup>15</sup> On drying, the washed precipitate shrinks much in bulk and is left in the bottom of the container in the form of a dark gray mass which explodes with the greatest violence on the slightest provocation. During the course of the work in preparing and analyzing the amide many tubes exploded without assignable cause, some of the explosions tearing holes through several layers of stout toweling wrapped around the tube for the protection of the operator. Attempts to deammonate silver amide to silver imide or nitride by warming the amide in vacuum were unsuccessful.<sup>15a</sup>

Silver amide dissolves readily in liquid ammonia solutions of ammonium nitrate, of ammonium iodide, and of certain acid amides as well as in excess of potassium amide. It may be hydrolyzed by very careful treatment with water vapor to silver oxide and ammonia.

**Gold Amide-Imide,  $\text{Au}(\text{NH})\text{NH}_2$ .** When potassium auribromide is treated with potassium amide in liquid ammonia solution an insoluble precipitate of the composition represented by the above formula is formed. The compound is highly explosive.<sup>16</sup>

<sup>14</sup> Sloan, *J. Am. Chem. Soc.*, **32**, 972 (1910).

<sup>15</sup> Franklin, *J. Am. Chem. Soc.*, **27**, 833 (1905).

<sup>15a</sup> The product long known as Berthollet's fulminating silver, which according to Raschig [*Ann. Chem.*, **233**, 93 (1886)] is silver nitride, has apparently never been established as such.

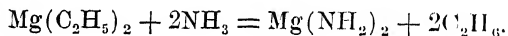
<sup>16</sup> Unpublished observations by G. S. Eohart.

**Beryllium Nitride,  $\text{Be}_3\text{N}_2$ .** By heating metallic beryllium in contact with either nitrogen or ammonia gas impure specimens of beryllium nitride have been obtained. Neither an amide nor an imide is known.<sup>17</sup>

**Magnesium Amide,  $\text{Mg}(\text{NH}_2)_2$ , and Magnesium Nitride,  $\text{Mg}_3\text{N}_2$**  Magnesium amide has been prepared by allowing sealed reaction tubes containing liquid ammonia and (1) metallic magnesium and sodium iodide, (2) magnesium and sodium amide, (3) magnesium and sodium ammonomagnesiate, and (4) magnesium and metallic sodium to stand for a few days or weeks with occasional shaking.<sup>1</sup>

Magnesium amide dissolves in liquid ammonia solutions of ammonium salts and is vigorously hydrolyzed by the action of water to magnesium hydroxide and water. When heated to a temperature around  $350^\circ$  to  $400^\circ$ , it loses ammonia and is converted into a product the composition of which lies between that of magnesium imide and magnesium nitride. As is familiarly known magnesium metal is energetically nitrized to the nitride when heated in contact with nitrogen or with ammonia gas.

Very recently Schlenk<sup>19</sup> has prepared magnesium amide by the action of ammonia on diethylmagnesium in ether solution,



He also prepared magnesium dianilide,  $\text{Mg}(\text{NHC}_6\text{H}_5)_2$ , by the interaction of diphenylmagnesium and aniline.

**Calcium Amide,  $\text{Ca}(\text{NH}_2)_2$  and Calcium Nitride,  $\text{Ca}_3\text{N}_2$ , Strontium Amide,  $\text{Sr}(\text{NH}_2)_2$ , and Strontium Nitride,  $\text{Sr}_3\text{N}_2$ , Barium Amide,  $\text{Ba}(\text{NH}_2)_2$ , and Barium Nitride,  $\text{Ba}_3\text{N}_2$ .**<sup>20</sup> The amides of calcium, strontium and barium have been prepared by the action of gaseous ammonia and of liquid ammonia on the respective metals. Barium amide has also been prepared by the action of ammonia on barium hydride and as a microcrystalline precipitate by the action of potassium amide on excess of barium nitrate in liquid ammonia solution. Bergstrom has obtained barium amide well crystallized by the action of metallic barium on liquid ammonia in the presence of metallic iron acting as catalyst. Barium amide is slightly soluble, calcium amide is practically insoluble in liquid ammonia. All three amides are energetically hydrolyzed by the action of water into the respective metallic hydroxides and ammonia.

The nitrides of calcium, strontium and barium are formed by

<sup>17</sup> Fichter and Brunner, *Z. anorg. Chem.*, **93**, 86 (1915); cf. Bergstrom, *J. Am. Chem. Soc.*, **50**, 655 (1928).

<sup>18</sup> Bergstrom, *J. Am. Chem. Soc.*, **48**, 2848 (1926).

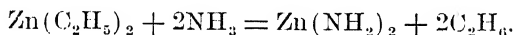
<sup>19</sup> Wihl. Schlenk, Jr., *Ber.*, **64**, 739 (1931).

<sup>20</sup> References are too numerous to be given here. Cf. Gmelin-Kraut, "Handb. anorg. Chem.," 8th ed., 1931.

heating the respective metals in contact with nitrogen and also by heating the amides. Whether inversely the nitrides may be ammonated to the amides, as has been reported, is not certainly known, at any rate Kraus and Hurd<sup>21</sup> were unable to confirm earlier observations to this effect. All three nitrides are hydrolyzed by the action of water into ammonia and the respective metallic hydroxides. Calcium ethylate, it is interesting to observe, has been obtained by the interaction of ethyl alcohol and calcium nitride.

Although the imides of calcium, strontium and barium have been reported, their existence, according to Kraus and Hurd, is open to doubt.

**Zinc Amide,  $\text{Zn}(\text{NH}_2)_2$ , and Zinc Nitride,  $\text{Zn}_3\text{N}_2$ .** Zinc amide was prepared many years ago by the action of ammonia on zinc ethyl.<sup>22</sup> Just as zinc ethyl is hydrolyzed by the action of water to zinc hydroxide and ethane so analogously it is ammonolyzed by the action of ammonia to zinc amide and ethane,



Zinc amide,<sup>22a</sup> which is practically insoluble in liquid ammonia, reacts with a solution of potassium amide to form potassium ammonozincate (cf. Chapter VII, p. 65), and with ammonium nitrate to form zinc nitrate. The zinc derivative of ethylamine of the formula,  $(\text{C}_2\text{H}_5\text{NH})_2\text{Zn}$ , has been obtained by the action of ethylamine on zinc diethyl.<sup>23</sup>

Zinc nitride is formed when zinc amide is heated to a temperature of low redness.<sup>24</sup> It is readily hydrolyzed to zinc hydroxide and ammonia by the action of water.

**Cadmium Amide,  $\text{Cd}(\text{NH}_2)_2$  and Cadmium Nitride,  $\text{Cd}_3\text{N}_2$ .** Bohart<sup>25</sup> obtained cadmium amide in the form of a colorless, amorphous precipitate by adding potassium amide to somewhat more than the equivalent amount of cadmium thiocyanate dissolved in liquid ammonia. It is interesting to note that the thoroughly washed cadmium amide precipitate shows the phenomenon of dispersion into the pure solvent. It reacts with water vapor to form cadmium hydroxide and ammonia. On heating cadmium amide to 180° it is converted into the black amorphous nitride.

**Mercuric Nitride,  $\text{Hg}_3\text{N}_2$ ,** is formed as a dense, brown precipitate when mercuric iodide, or bromide, in liquid ammonia solution is

<sup>21</sup> Kraus and Hurd, *J. Am. Chem. Soc.*, **45**, 2559 (1923).

<sup>22</sup> Frankland, *J. prakt. Chem.*, [1] **73**, 35 (1858).

<sup>22a</sup> Fitzgerald, *J. Am. Chem. Soc.*, **29**, 656 (1907).

<sup>23</sup> Gal, *Bull. soc. chim.*, [2] **39**, 583 (1883).

<sup>24</sup> Frankland, *Phil. Mag.*, [4] **15**, 149 (1858).

<sup>25</sup> Bohart, *J. Phys. Chem.*, **19**, 545 (1915). Cf. Henderson and Gallety, *J. Soc. Chem. Ind.*, **27**, 387 (1908); Fischer and Schröter, *Ber.*, **43**, 1465 (1910).



run into an excess of potassium amide dissolved in the same solvent.<sup>26</sup> It dissolves readily in liquid ammonia solutions of ammonium bromide, iodide or nitrate and slowly in potassium amide solution, in the latter case undoubtedly to form potassium ammonio-mercurate, though such a salt has not been isolated. The dry compound—that is to say free from ammonia and of course from water—detonates violently by impact or on being brought into contact with liquid water. The product formed by the action of water vapor on mercuric nitride is converted into mercuric chloride and ammonium chloride by the action of dilute hydrochloric acid.

Pesci<sup>27</sup> prepared a compound to which he gave the formula:  $\text{Hg}(\text{NHC}_6\text{H}_5)_2$ , which may be looked upon as a diphenyl derivative of mercuric amide while Dimroth's<sup>28</sup> compound,  $\text{HgNC}_6\text{H}_5$ , may be said to be a phenyl derivative of mercuric imide or aniline in which both amino hydrogen atoms are replaced by mercury.

**Ammonous Aluminum Nitride,  $\text{AlN} \cdot x\text{NH}_3$  and Aluminum Nitride,  $\text{AlN}$ .**<sup>29</sup> When to a liquid ammonia solution of sodium ammonoaluminate an equivalent quantity of ammonium bromide is added a bulky, amorphous precipitate of ammonous aluminum nitride is formed which simulates in a remarkably close manner the familiar behavior of hydrous aluminum oxide. Standing in contact with liquid ammonia at laboratory temperature the precipitate starting with a composition lying between that of aluminum amide  $\text{Al}(\text{NH}_2)_3$ , and aluminum imide-amide,  $\text{Al}(\text{NH})\text{NH}_2$ , continuously loses ammonia during a period of days or weeks at the end of which time its composition is that of a mixture of much aluminum imide  $\text{Al}_2(\text{NH})_3$ , and little aluminum nitride. On removing the solvent and heating the precipitate in vacuum, first at  $220^\circ$  to  $240^\circ$  and then at  $380^\circ$ , deammonation continues but so slowly that the ammonous nitride can not be completely converted into aluminum nitride within a reasonable time. It is fair to assume that complete deammonation could be quickly accomplished at a higher temperature.

Ammonous aluminum nitride dissolves readily in liquid ammonia solutions of ammonium bromide to form aluminum bromide, or of potassium amide to form potassium ammonoaluminate. It is vigorously hydrolyzed to hydrous aluminum oxide and ammonia by the action of water.

Aluminum nitride is formed when metallic aluminum is strongly heated in an atmosphere of nitrogen or of ammonia, and by passing

<sup>26</sup> Fitzgerald, *J. Am. Chem. Soc.*, **27**, 839 (1905). Cf. Hirzel, *Jahrb.*, **8**, 41 (1852); Plantamour, *Ann. Chem.*, **40**, 115 (1841).

<sup>27</sup> Pesci, *Z. anorg. Chem.*, **15**, 213 (1897).

<sup>28</sup> Dimroth, *Ber.*, **35**, 2043 (1902).

<sup>29</sup> Bergstrom, *J. Phys. Chem.*, **32**, 434 (1925).

nitrogen over a mixture of aluminum oxide and carbon at a high temperature.

**Thallous Nitride,  $Tl_3N$ .** This nitride is formed as a dense, black precipitate when equivalent quantities of thallous nitrate and potassium amide are brought together in liquid ammonia solution.<sup>30</sup> It dissolves readily in a liquid ammonia solution of ammonium nitrate to form thallous nitrate and in potassium amide solution to form potassium ammonothallite. (Cf. Chapter VII, p. 71.) It explodes with violence when heated or subjected to shock or when brought into contact with liquid water. In contact with water vapor it is hydrolyzed to thallous hydroxide and ammonia.

**Lead Imide,  $PbNH$ ,** is obtained in the form of an orange-red precipitate when lead iodide, or any other soluble lead salt, and potassium amide are brought together in equivalent quantities in liquid ammonia solution.<sup>31</sup>

Lead imide dissolves readily in liquid ammonia solutions of ammonium iodide or nitrate and also in an excess of potassium amide. It explodes violently when heated or on coming in contact with liquid water. It hydrolyzes quietly in contact with water vapor to lead hydroxide and ammonia.

**Bismuth Nitride,  $BiN$ .** When bismuth bromide or iodide in solution in liquid ammonia is run into an excess of potassium amide a dark brown precipitate of bismuth nitride, or possibly of an ammonous nitride, is formed. On drying the precipitate, that is, freeing it from ammonia, it blackens markedly and at the same time undergoes a certain amount of decomposition as is shown by the fact that the ammonia-free product contains a small amount of metallic bismuth. On heating bismuth nitride or on bringing it into contact with liquid water it explodes violently. It is hydrolyzed by the action of water vapor. It dissolves in liquid ammonia solutions of ammonium bromide or iodide but is apparently insoluble in potassium amide solution.

**Molybdenum Nitride,  $Mo_3N_2$ ,** has been obtained in the form of a powder showing metallic luster by heating molybdenum trichloride in a current of ammonia gas.<sup>32</sup> It is formed also by heating molybdenum pentachloride, or molybdic acid, at a bright red heat in contact with ammonia.

Attempts to prepare an amide of molybdenum by the action of potassium amide, in liquid ammonia solution, on molybdenum tribromide yielded ammonobasic mixtures of indefinite composition.<sup>33</sup>

**Manganese Amide,  $Mn(NH_2)_2$ .** This amide is obtained in the

<sup>30</sup> Franklin, *J. Phys. Chem.*, **16**, 683 (1912).

<sup>31</sup> Franklin, *J. Am. Chem. Soc.*, **27**, 842 (1915); *J. Phys. Chem.*, **15**, 509 (1911).

<sup>32</sup> Rosenheim and Braun, *Z. anorg. Chem.*, **46**, 311 (1905).

<sup>33</sup> Bergstrom, *J. Am. Chem. Soc.*, **47**, 2323 (1925).

form of a pale yellow, noncrystalline precipitate contaminated with more or less potassium ammonohypomanganite (*cf.* Chapter VII) when potassium amide is added to an excess of manganese thiocyanate in liquid ammonia solution.<sup>34</sup> Heated at 140° in vacuum manganese amide loses ammonia and nitrogen and is converted into a black product which is either an ammonous nitride of indefinite composition or a mixture of manganese imide and nitride. Manganese amide is vigorously hydrolyzed by the action of water to manganese hydroxide and ammonia, small quantities of nitrogen and hydrogen being evolved at the same time. The imide-nitride mixture is scarcely affected by water, but dissolves slowly in dilute sulfuric acid.

A manganese nitride approximating in composition the formula  $Mn_3N_2$ , has been obtained by heating metallic manganese at 800° in a current of ammonia.<sup>35</sup>

**Ferrous Nitride.** None of the attempts to prepare a nitride of iron of definite composition has been successful.<sup>36</sup>

By digesting the black precipitate formed by the action of potassium amide on ferrous bromide with a liquid ammonia solution of ammonium thiocyanate Bergstrom obtained preparations approximately of the composition,  $Fe_3N_2$ . Attempts to prepare an ammonoferrite of potassium were unsuccessful.

**Nickel Amide,  $Ni(NH_2)_2$ , and Nickel Nitride,  $Ni_3N_2$ .** Nickel amide has been obtained in the form of a flocculent, reddish precipitate by the action of potassium amide on an excess of nickel thiocyanate in liquid ammonia solution.<sup>37</sup> Toward the end of the washing process carried out in purifying the amide preparatory to analysis Bohart noted its tendency to pass into the colloidal state when in contact with pure solvent. It dissolves in a liquid ammonia solution of ammonium nitrate to form nickel nitrate and reacts mildly with water, being thereby hydrolyzed into nickel hydroxide and ammonia.

When nickel amide is heated in vacuum at 120° ammonia mixed with small amounts of hydrogen and nitrogen is given off leaving a black, amorphous nickel nitride mixed with more or less metallic nickel. Nickel nitride is scarcely attacked by water but dissolves in dilute hydrochloric acid to form nickel chloride and ammonium chloride.

**Ammonous Cobaltous Nitride,  $Co_3N_2 \cdot xNH_3$ , and Cobaltous Ni**

<sup>34</sup> Bergstrom, *J. Am. Chem. Soc.*, **46**, 1555 (1924).

<sup>35</sup> Henderson and Gallety, *J. Soc. Chem. Ind.*, **27**, 388 (1908).

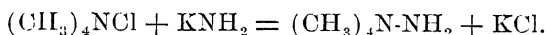
<sup>36</sup> Fowler, *J. Chem. Soc.*, **79**, 285 (1901); White and Kirschbaum, *J. Am. Chem. Soc.*, **28**, 1343 (1906); Bergstrom, *J. Am. Chem. Soc.*, **46**, 2635 (1924).

<sup>37</sup> Bohart, *J. Phys. Chem.*, **19**, 561 (1914).

tride,  $\text{Co}_3\text{N}_2$ .<sup>38</sup> When potassium amide is added to a liquid ammonia solution of cobaltous thiocyanate a bright blue, flocculent precipitate approximately of the composition of cobaltous amide is formed. On standing in contact with the solution this precipitate gradually loses ammonia and becomes black. This black product when heated in vacuum at  $120^\circ$  is converted into cobaltous nitride. The amide reacts vigorously with water, the nitride very sluggishly.

The behavior of the blue precipitate of ammonous cobaltous nitride resembles in a striking manner that of hydrous cupric oxide which compound of indefinite composition, it will be recalled, undergoes dehydration on standing in contact with water but is converted definitely into cupric oxide only when heated in the dry state to a relatively high temperature. Attempts made by Bergstrom to prepare a potassium ammonocobaltite were unsuccessful.

**Attempts to Prepare Tetramethylammonium Amide.** Since potassium chloride is but slightly soluble in liquid ammonia it was surmised that this salt would be precipitated leaving tetramethylammonium amide in solution on bringing together solutions of equimolecular quantities of tetramethylammonium chloride and potassium amide. Potassium chloride separates from solution in agreement with a reaction represented by the equation,



However the solution was found to contain trimethylamine and methylamine instead of tetramethylammonium amide. Obviously the ammono base breaks down at laboratory temperature as soon as formed, in a manner analogous to the decomposition which tetramethylammonium hydroxide undergoes at higher temperatures.

Similar unsuccessful attempts have been made to prepare trimethylsulfonium amide,  $(\text{CH}_3)_3\text{S-NH}_2$ , and diphenyliodonium amide,  $(\text{C}_6\text{H}_5)_2\text{I-NH}_2$ , the ammonia analogs respectively of trimethylsulfonium hydroxide,  $(\text{CH}_3)_3\text{S-OH}$ , and diphenyliodonium hydroxide,  $(\text{C}_6\text{H}_5)_2\text{I-OH}$ . The first of the two hypothetical amides presumably breaks down into dimethylsulfide and methylamine, the other into phenyl iodide and methylamine.<sup>39</sup>

<sup>38</sup> Bergstrom, *J. Am. Chem. Soc.*, **46**, 2631 (1924); *J. Phys. Chem.*, **32**, 433 (1928).

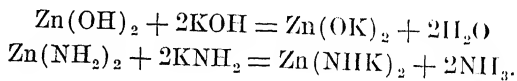
<sup>39</sup> Unpublished observations.

## CHAPTER VII.

### ALKALI METAL SALTS OF AMPHOTERIC METALLIC AMIDES AND IMIDES.

Among the phenomena with which the student of chemistry early becomes familiar is the solubility of the hydroxides of zinc, aluminum and lead in solutions of potassium hydroxide. In connection with his observations he occasionally asks why amphoteric properties are shown by these particular metallic hydroxides and not by others with which he is familiar. Whatever may be the answer to this question we shall find as we proceed that while on the one hand only a limited number of metallic hydroxides dissolves in aqueous solutions of potassium hydroxide, on the other, the large majority of metallic amides and imides shows amphoteric properties in that they react with potassium amide in solution in liquid ammonia to form compounds which are to be looked upon as derivatives of ammonia in the same sense that potassium zincate, for example, is a derivative of water.

Fitzgerald<sup>1</sup> found that just as an aqueous solution of potassium hydroxide dissolves zinc hydroxide to form the aquozincate of potassium, so potassium amide in liquid ammonia solution acts on zinc amide to form a crystalline product which must be looked upon as an ammonozincate of potassium. The closely analogous reactions taking place in the respective solvents, water and ammonia may be represented by the equations,



Neither of the compounds represented by the respective formula  $\text{Zn(OK)}_2$  and  $\text{Zn(NHK)}_2$  is known. Just as such aquozincates are known, so have been isolated always contain "water of crystallization"<sup>2</sup> so Fitzgerald's compound, which was found to have the empirical composition  $\text{ZnN}_4\text{H}_8\text{K}_2$ , may be looked upon as an ammonozincate of po-

<sup>1</sup> Fitzgerald, *J. Am. Chem. Soc.*, 29, 656 (1907).

<sup>2</sup> Comey and Jackson, *Am. Chem. J.*, 11, 145 (1889); Foerster and Gunther, *Z. Elektrochem.*, 6, 301 (1900); Hantzsch, *Z. anorg. Chem.*, 30, 289 (1903); Wood, *J. Chem. Soc.*, 97, 878 (1910); Goudriaan, *Chem. Abstracts*, 14, 66 (1920).

tassium combined with "ammonia of crystallization" and given the formula  $\text{Zn}(\text{NHK})_2 \cdot 2\text{NH}_3$ .

Fitzgerald's success in preparing beautifully crystallized specimens of potassium ammonozincate of sharply definite composition together with early observations made in this laboratory showing that salts of many metals in solution in liquid ammonia, when treated with potassium amide, give precipitates which dissolve on adding the precipitant in excess, led to a series of investigations planned to determine the extent to which the formation of salts by the action of potassium amide on the amides, imides and nitrides of other metals might be carried. The result of these investigations has been to show that a large number of metallic amides, including those of such strongly positive metals as magnesium, barium, strontium, calcium and even sodium and lithium, react with potassium amide to form compounds which must be looked upon as salts in which these metals play a part closely similar to that which zinc plays in potassium aquozincate and which lead and aluminum play in the compounds formed by the action of aqueous potassium hydroxide on the hydroxides of these metals.<sup>3</sup>

A list of compounds which may be regarded as alkali metal salts of amphoteric metallic amides and imides follows. All these compounds have been prepared by reactions carried out in liquid ammonia solutions, whence it follows that statements concerning precipitation, crystallization, washing, drying and so forth, unless otherwise specifically stated, have to do with operations in which liquid ammonia was used as solvent.

**Potassium Ammonozincate,  $\text{Zn}(\text{NHK})_2 \cdot 2\text{NH}_3$ .<sup>4</sup>** The formation of

<sup>3</sup> It is fair to assume that the well-known solubility of many metals [Le Blanc and Bergmann, *Ber.*, **42**, 4728 (1909) and Le Blanc and Weyl, *Ber.*, **45**, 2300 (1912)] and metallic hydroxides in fused potassium hydroxide is accompanied by salt formation. Certainly the existence of the long list of compounds described in the following pages lends considerable support to the view that in these potassium hydroxide fusions the water analogs of our ammono salts are present. Some observations made in this laboratory on the solubility of metals and metallic oxides in fused potassium hydroxide gave the following results. The oxides of barium, strontium, calcium, magnesium, zinc, cadmium, mercury and silver dissolve to clear colorless fusions. Cupric oxide gives a fusion which is blue at lower and brown at higher temperatures. Nickel oxide gives a purple solution which changes to brown at high temperatures. Ferric oxide gives a purple melt when dilute, more concentrated solutions are very dark. Bismuth oxide dissolves abundantly to form a deep orange-colored melt. Magnesium and calcium dissolve in fused potassium hydroxide with evolution of hydrogen. Metallic platinum gives a clear yellow solution. Palladium dissolves from the palladium gold alloy known as palau to form a green solution leaving the interior of the crucible yellow from exposed gold.

<sup>4</sup> This compound may be represented as a potassium ammonozincate containing ammonia of crystallization as above or it may be given the formula  $\text{Zn}(\text{NH}_2)_2 \cdot 2\text{KNH}_2$ , in accordance with which it is a molecular compound of zinc amide and potassium amide or, following Werner ["Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," 3rd ed., 123 (1913)], it may be given the formula  $\text{Zn}[(\text{NH}_2)_4]\text{K}_2$ . Most of the compounds described in the following pages may be given similar alternate formulas.

this compound by the action of potassium amide on zinc amide has already been discussed. It is interesting to note that Fitzgerald prepared the same compound by the action of a solution of potassium amide on metallic zinc,  $\text{Zn} + 2\text{KNH}_2 = \text{Zn}(\text{NHK})_2 + \text{H}_2$ .

Potassium ammonozincate is most conveniently obtained by the action of potassium amide on tetrammonated zinc iodide in accordance with the equation,



Zinc iodide when brought into contact with liquid ammonia forms the slightly soluble tetrammonate which, under the action of potassium amide, is gradually converted into a mass of well-formed crystals of the slightly soluble potassium ammonozincate. At temperatures above  $160^\circ$  the salt loses ammonia without however giving a well-defined deammonation product. At higher temperatures deep seated decomposition takes place.

Although the aquozincate and the ammonozincate of potassium are strictly analogous compounds their behavior, the one toward water and the other toward liquid ammonia, are in striking contrast. The ammono salt is entirely stable in the presence of liquid ammonia, showing no tendency to undergo ammonolysis, whereas the aquo salt is highly hydrolyzed in water solution even in the presence of a large excess of potassium hydroxide. The explanation of this difference in behavior of the two salts toward the respective solvents is to be found in the very marked difference in solvolyzing power of liquid ammonia as compared with water, to which attention has already been called.

Potassium Ammonoplumbite,  $\text{PbNK} \cdot 2\frac{1}{2}\text{NH}_3$ ,  $\text{PbNK} \cdot 2\text{NH}_3$  and  $\text{PbNK} \cdot \text{NH}_3$ .<sup>6</sup> Lead imide, obtained in the form of a reddish-yellow precipitate by the action of potassium amide on lead iodide, dissolves readily in excess of potassium amide to form a solution from which, by proper adjustment of concentration and temperature, a beautifully crystallized product of the composition represented by the first of the above formulas may be obtained. In vacuum at low temperatures this colorless compound loses one half molecule of ammonia, thereby giving a product which has the appearance of an effloresced salt. When this partially deammonated salt is heated to  $80^\circ$  to  $100^\circ$  additional ammonia is given off leaving a more or less discolored product of the composition represented by the formula,  $\text{PbNK} \cdot \text{NH}_3$ . At temperatures around  $150^\circ$  the compound explodes, as it does also at laboratory temperatures when brought

<sup>5</sup> Franklin, *J. Am. Chem. Soc.*, 29, 274 (1907).

<sup>6</sup> Franklin, *J. Phys. Chem.*, 15, 509 (1911).

into contact with water or dilute acid. Exposed to the action of water vapor the salt quietly undergoes hydrolysis to form lead hydroxide, potassium hydroxide and ammonia.

According to Hantzsch<sup>6a</sup> the compound formed by dissolving lead hydroxide in aqueous sodium hydroxide, instead of being sodium plumbite, is rather a sodium plumboformate of the formula,  $\text{HPbOONa}$ . Following Hantzsch, which however the writer is rather disinclined to do, the compounds described above become potassium plumboformates of the respective formulas,  $\text{HPb}(\text{NH}_2)_2\text{NHK} \cdot \frac{1}{2}\text{NH}_3$  or  $\text{HPb}(\text{NH})\text{NHK} \cdot 1\frac{1}{2}\text{NH}_3$ ,  $\text{HPb}(\text{NH}_2)_2\text{NHK}$  or  $\text{HPb}(\text{NH})\text{NHK} \cdot \text{NH}_3$  and  $\text{HPb}(\text{NH})\text{NHK}$ .

Potassium Ammonoaluminate,  $\text{Al}(\text{NH})\text{NHK} \cdot 2\text{NH}_3$ , and  $\text{Al}(\text{NH})\text{NHK} \cdot \text{NH}_3$ .<sup>7</sup> Metallic aluminum, presumably because of the presence of an insoluble protective film covering the surface of the metal, is not attacked by a solution of potassium amide. The amalgamated metal however dissolves readily to form a very soluble potassium ammonoaluminate which separates from the cold concentrated solution in the form of colorless, needle-like crystals. Dried in vacuum at low temperatures the compound has the composition represented by the first formula given above. At  $55^\circ$  in vacuum the salt melts and loses one molecule of ammonia forming a product of the composition represented by the second formula. When the very soluble crystallized salt is brought into contact with pure liquid ammonia it does not dissolve completely. An amorphous precipitate, presumably of ammonous aluminum nitride,  $\text{AlN} \cdot x\text{NH}_3$ , formed by the ammonolysis of potassium ammonoaluminate, settles to the bottom of the reaction tube. This insoluble material dissolves on the addition of a small amount of potassium amide or when the liquid ammonia is largely evaporated away.

Bergstrom<sup>8</sup> has shown that the action of potassium amide (in solution in liquid ammonia) on metallic aluminum takes place in two steps. Metallic potassium and aluminum amide or ammonous aluminum nitride are first formed in accordance with the equation,  $\text{Al} + 3\text{KNH}_2 = 3\text{K} + \text{Al}(\text{NH}_2)_3$ , following which the aluminum amide dissolves in the excess of potassium amide to form potassium ammonoaluminate.

Potassium ammonoaluminate is also formed by the action of a solution of metallic potassium on amalgamated aluminum. Ammonia and metallic potassium interact with a fair degree of speed in the presence of aluminum acting as a catalyst. The potassium

<sup>6a</sup> Hantzsch, *Z. anorg. Chem.*, **30**, 308 (1902).

<sup>7</sup> Bergstrom, *J. Am. Chem. Soc.*, **46**, 1545 (1924).

<sup>8</sup> Bergstrom, *J. Am. Chem. Soc.*, **45**, 2792 (1923); Kraus, *J. Am. Chem. Soc.*, **44**, 1224 (1922).



amide thus formed then reacts with metallic aluminum as explained above. Bergstrom makes the interesting suggestion that the initial step in the action of aqueous potassium hydroxide on such metal as zinc, aluminum and magnesium consists in the separation of free alkali metal which is of course immediately reconverted into the hydroxide in the presence of water. It may be noted in this connection that a blue area, presumably a solution of metallic potassium in potassium hydroxide, is developed around the end of a rod of metallic magnesium immersed in fused potassium hydroxide. According to Bergstrom free potassium is formed in accordance with the equation,  $\text{Mg} + 2\text{KOH} = \text{Mg}(\text{OK})_2 + 2\text{K}$ .

**Sodium Ammonoaluminate**,  $\text{Al}(\text{NH})\text{NHNa} \cdot 2\text{NH}_3$  and  $\text{Al}(\text{NH})\text{NHNa} \cdot \text{NH}_3$ . A well-crystallized product of the composition represented by the first formula was obtained by Bergstrom by concentrating and cooling the solution formed by the action of sodium amide, or of metallic sodium, on amalgamated aluminum. When heated in vacuum at  $80^\circ$  the salt melts and simultaneously loses one molecule of ammonia. The resulting product has the composition represented by the second formula.

**Lithium Ammonoaluminate**,  $\text{Al}(\text{NH})\text{NHLi} \cdot 2\text{NH}_3$ . Bergstrom obtained this compound in the form of slightly soluble crystals by the very slow action of lithium amide on amalgamated aluminum.

**Potassium Ammonoberylliate**,  $\text{BeNK} \cdot 2\text{NH}_3$  and  $\text{BeNK} \cdot \text{NH}_3$ ,<sup>9</sup> has been obtained by dissolving beryllium in a solution of potassium amide and also by allowing a solution containing metallic potassium to stand in contact with metallic beryllium. The diammonated salt which separates from cold very concentrated solutions, loses one molecule of ammonia when heated in vacuum at  $180^\circ$ . Potassium ammonoberylliate is vigorously hydrolyzed by the action of water to potassium hydroxide, beryllium hydroxide and ammonia.

**Sodium Ammonoberylliate**,  $\text{BeNNa} \cdot 2\text{NH}_3$  and  $\text{BeNNa} \cdot \text{NH}_3$ . The diammonated salt which Bergstrom prepared by the action of a solution of metallic sodium on metallic beryllium, closely resembles the corresponding potassium salt. When heated in vacuum it loses one molecule of ammonia.

**Potassium Ammonomagnesiate**,  $\text{Mg}(\text{NHK})_2 \cdot 2\text{NH}_3$ .<sup>10</sup> This salt has been prepared by the action of potassium amide in solution in liquid ammonia, first, on a halogen salt of magnesium, second, on an aquo acid salt, third, on an aquo-ammonio acid salt and, finally on metallic magnesium itself, in accordance with reactions represented by the respective equations,

<sup>9</sup> Bergstrom, *J. Am. Chem. Soc.*, **50**, 652 (1928).

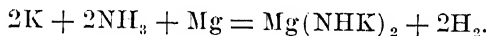
<sup>10</sup> Franklin, *J. Am. Chem. Soc.*, **35**, 1455 (1913); Bergstrom, *ibid.*, **48**, 2848 (1926).

- (1)  $\text{MgI}_2 + 4\text{KNH}_2 = \text{Mg}(\text{NHK})_2 + 2\text{KI} + 2\text{NH}_3$
- (2)  $\text{Mg}(\text{NO}_3)_2 + 4\text{KNH}_2 = \text{Mg}(\text{NHK})_2 + 2\text{NH}_3 + 2\text{KNO}_3$
- (3)  $(\text{CH}_3\text{CONH})_2\text{Mg} + 4\text{KNH}_2 = \text{Mg}(\text{NHK})_2 + 2\text{NH}_3 + 2\text{CH}_3\text{CONHK}$
- (4)  $\text{Mg} + 2\text{KNH}_2 = \text{Mg}(\text{NHK})_2 + \text{H}_2$ .

It may be assumed that potassium amide acts on the respective salts to form the practically insoluble magnesium amide which latter compound then reacts with excess of potassium amide to form potassium ammonomagnesiate. According to Bergstrom the formation of potassium ammonomagnesiate by the action of potassium amide on metallic magnesium takes place in two steps as represented by the equations,

- (1)  $\text{Mg} + 2\text{KNH}_2 = \text{Mg}(\text{NH}_2)_2 + 2\text{K}$
- (2)  $\text{Mg}(\text{NH}_2)_2 + 2\text{KNH}_2 = \text{Mg}(\text{NH}_2)_2 \cdot 2\text{KNH}_2$ .

Potassium ammonomagnesiate is also formed by the action of a solution of potassium on metallic magnesium,



Potassium ammonomagnesiate has been obtained in the form of a crystalline powder which is but slightly soluble in liquid ammonia. It is converted into a mixture of potassium nitrate and magnesium nitrate by the action of a liquid ammonia solution of ammonium nitrate and is hydrolyzed on treatment with water into potassium hydroxide, magnesium hydroxide and ammonia.

**Sodium Ammonomagnesiate**,  $\text{Mg}(\text{NHNa})_2 \cdot 2\text{NH}_3$ .<sup>11</sup> When metallic sodium or sodium amide in the presence of liquid ammonia is allowed to stand in contact with metallic magnesium a product consisting of a mixture of sodium ammonomagnesiate and magnesium amide is obtained. By repeatedly extracting the mixture with liquid ammonia Bergstrom obtained the somewhat soluble (6 grams per liter at 20°) sodium ammonomagnesiate in a state of purity.

**Potassium Ammonocadmiate**,  $\text{Cd}(\text{NHK})_2 \cdot 2\text{NH}_3$ .<sup>12</sup> This compound, in the form of an amorphous precipitate, has been prepared by the action of an excess of potassium amide on the very slightly soluble cadmium amide and also on the readily soluble potassium cyanocadmiate.

**Potassium Ammonohypomanganite**,  $\text{Mn}(\text{NHK})_2 \cdot 2\text{NH}_3$ .<sup>13</sup> Berg-

<sup>11</sup> Bergstrom, *J. Am. Chem. Soc.*, **48**, 2852 (1926).

<sup>12</sup> Bohart, *J. Phys. Chem.*, **19**, 542 (1914).

<sup>13</sup> Bergstrom, *J. Am. Chem. Soc.*, **46**, 1552 (1924).

strom obtained this compound in the form of a light yellow, crystalline precipitate by the action of potassium amide on metallic manganese, of metallic potassium on metallic manganese and of potassium amide on manganese thiocyanate in accordance with reactions which in the light of the preceding discussions will be familiar. When potassium ammonomanganite is heated to a temperature above  $110^{\circ}$  to  $120^{\circ}$  it yields ammonia, nitrogen, hydrogen and a black residue of indefinite composition. Potassium ammonohypomanganite in the dry state is pyrophoric.

**Sodium Ammonohypomanganite**,  $\text{Mn}(\text{NHNa})_2 \cdot 2\text{NH}_3$ .<sup>14</sup> Sodium amide in solution in liquid ammonia slowly attacks metallic manganese giving a light yellow, crystalline product which is distinctly more soluble than is potassium ammonohypomanganite. Its properties are very similar to those of the potassium salt.

**Lithium Ammonoferrate**,  $\text{LiN} \cdot \text{Fe} \cdot \text{N} \cdot \text{Li}_2$ .<sup>15</sup> By heating a mixture of lithium nitride and metallic iron, both finely pulverized, in an atmosphere of nitrogen the iron is nitridized to the ferric state and forms with the lithium nitride a definite compound of the composition represented by the above formula. The compound is vigorously hydrolyzed by the action of water to ferric hydroxide, lithium hydroxide and ammonia.

Attempts by Bergstrom<sup>16</sup> to prepare a potassium ammonoferrite by the action of potassium amide in excess on ferrous bromide were unsuccessful.

**Potassium Ammononickelate**,  $\text{K}_2\text{N} \cdot \text{Ni} \cdot \text{N}(\text{K}) \cdot \text{Ni} \cdot \text{NK}_2 \cdot 6\text{NH}_3$ ,  $2\text{Ni}(\text{NH}_2)_2 \cdot 5\text{KNH}_2$ . Bohart found that when nickel thiocyanate, in liquid ammonia solution, is treated with an excess of potassium amide a deep red solution is formed from which a red, crystalline product is slowly deposited. The salt, which is slightly soluble, was obtained well crystallized and of sharply definite composition. It is formulated above as a hexammonated salt of an unknown dinickel diamide-imide,  $\text{H}_2\text{N} \cdot \text{Ni} \cdot \text{NH} \cdot \text{Ni} \cdot \text{NH}_2$ , and as a molecular compound of two molecules of nickel amide with five molecules of potassium amide.

In his attempts to prepare nickel amide and an ammononickelate by the action of potassium amide on the potassium nickel cyanide,  $\text{Ni}(\text{CN})_2 \cdot 2\text{KCN}$ , Bohart obtained the compounds represented by the respective formulas,  $2\text{KCN} \cdot 2\text{Ni}(\text{CN})_2 \cdot \text{Ni}(\text{NHK})_2 \cdot 8\text{NH}_3$ ,  $2\text{KCN} \cdot 2\text{Ni}(\text{CN})_2 \cdot \text{Ni}(\text{NHK})_2$ ,  $2\text{KCN} \cdot \text{Ni}(\text{CN})_2 \cdot \text{Ni}(\text{NHK})_2$  and  $\text{Ni}(\text{CN})_2 \cdot 2\text{Ni}(\text{NHK})_2 \cdot 3\text{KNH}_2 \cdot 4\text{NH}_3$ . The nature of these compounds remains unexplained.

**Potassium Ammonocuprite**,  $\text{CuNK}_2 \cdot 3\text{NH}_3$ ,  $\text{CuNK}_2 \cdot 2\text{NH}_3$  and

<sup>14</sup> Bergstrom, *J. Am. Chem. Soc.*, **48**, 2882 (1926).

<sup>15</sup> Frankenburger, Andrusso and Dürr, *Z. Electrochem.*, **34**, 632 (1928).

<sup>16</sup> Bergstrom, *J. Am. Chem. Soc.*, **46**, 2634 (1924).

$\text{CuNK}_2.1\frac{1}{3}\text{NH}_3$ .<sup>17</sup> The precipitate formed when equivalent quantities of cupric nitrate and potassium amide are brought together in liquid ammonia solution is an ammonous cuprous nitride roughly of the composition of cuprous imide. When this precipitate is treated with a solution of potassium amide it dissolves to form potassium ammonocuprite,  $\text{Cu}_2\text{NH} + 4\text{KNH}_2 = 2\text{CuNK}_2 + 4\text{NH}_3$ . From the concentrated, cold solution the very soluble, deliquescent (in the sense that the product liquefies in an atmosphere of gaseous ammonia in equilibrium with liquid ammonia at laboratory temperatures) salt of the composition represented by the first formula above separates as a crop of colorless crystals. This triammonated salt loses one molecule of ammonia in vacuum at  $20^\circ$  and at  $160^\circ$  gives a black product of the composition represented by the formula,  $\text{CuNK}_2.1\frac{1}{3}\text{NH}_3$  or  $\text{Cu}_3\text{N}.6\text{KNH}_2$ .<sup>18</sup> This black mass dissolves in liquid ammonia to form a colorless solution from which the triammonated salt may again be crystallized. A liquid ammonia solution of ammonium nitrate added to a solution of potassium ammonocuprite gives a colorless precipitate of ammonous cuprous nitride which on further addition of the acid dissolves to a colorless solution of cuprous nitrate. Treated with dilute aqueous nitric acid potassium ammonocuprite is converted into a mixture of cuprous nitrate, potassium nitrate and ammonium nitrate. Dilute aqueous sulfuric acid forms cupric sulfate, metallic copper, potassium sulfate and ammonium sulfate.

**Potassium Ammonoargentate**,  $\text{AgNHK.NH}_3$ .<sup>19</sup> Silver amide, which is formed as a white precipitate when potassium amide is added to silver nitrate in liquid ammonia solution, dissolves in excess of potassium amide to form potassium ammonoargentate as represented by the equation,  $\text{AgNH}_2 + \text{KNH}_2 = \text{AgNHK} + \text{NH}_3$ . The salt separates from concentrated solutions as well-formed crystals which withstand a temperature of  $100^\circ$  or more without change. Heated to higher temperatures it decomposes vigorously but without explosive violence. Nor does it explode when brought into contact with water or dilute acid. This behavior is in interesting contrast with that of silver amide which explodes violently on the slightest provocation.

Liquid ammonia solutions of acids act on potassium ammonoargentate precipitating silver amide which dissolves on further addition of the acid to form the silver and potassium salts of the acid used.

**Potassium Ammonothallite**,  $\text{TlNK}_2.4\text{NH}_3$ ,  $\text{TlNK}_2.2\text{NH}_3$  and

<sup>17</sup> Franklin, *J. Am. Chem. Soc.*, **34**, 1501 (1912).

<sup>18</sup> The analytical data given by Franklin are in better agreement with this formula than with the formula,  $\text{CuNK}_2.\text{NH}_3$ .

<sup>19</sup> Franklin, *J. Am. Chem. Soc.*, **37**, 854 (1915).

$\text{TlNK}_2.1\frac{1}{3}\text{NH}_3$ .<sup>20</sup> Black thallium nitride dissolves in a solution of potassium amide to form potassium ammonothallite in accordance with the equation,  $\text{Tl}_3\text{N} + 6\text{KNH}_2 = 3\text{TlNK}_2 + 4\text{NH}_3$ . From the solution thus obtained beautiful yellow crystals of a salt of the composition represented by the first of the above formulas may be separated by cooling the solution at proper concentration. The tetrammonate loses two molecules of ammonia when heated in vacuum to laboratory temperatures and an additional two-thirds of a molecule as the temperature approaches 100°. The diammonated salt presents the appearance of an effloresced salt. The final black product represented by the third formula above, or perhaps better by the formula,  $\text{Tl}_3\text{N}.6\text{KNH}_2$ , undergoes gradual decomposition at temperatures around 100°. At somewhat higher temperatures it explodes. The tetrammonated salt is also explosive. Even so mild a shock as that brought about by the falling of a tube containing the salt through a few feet on to a wood floor results in a violent explosion. Potassium ammonothallite is decomposed by liquid ammonia solutions of acids. Ammonium nitrate for example added to a solution of the salt precipitates first thallous nitride which latter on further addition of acid goes into solution as thallous nitrate.

**Potassium Ammonobarate**,  $\text{BaNK}.2\text{NH}_3$ .<sup>21</sup> When a soluble barium salt and potassium amide in excess are brought together in liquid ammonia solution a precipitate of the composition represented by the above formula is formed. As thus obtained potassium ammonobarate is an amorphous or at best a micro-crystalline product which remains unchanged on exposure to temperatures around 100°. It dissolves in a liquid ammonia solution of ammonium nitrate and is vigorously hydrolyzed by the action of water to barium hydroxide, potassium hydroxide and ammonia.

**Potassium Ammonostrontiate**,  $\text{SrNK}.2\text{NH}_3$ . This salt has been obtained by following a procedure similar to that described above for the preparation of potassium ammonobarate. It closely resembles the ammonobarate in appearance and behavior.

**Potassium Ammonocalciate**,  $\text{CaNK}.2\text{NH}_3$ , has been prepared by the action of potassium amide in liquid ammonia solution on metallic calcium and by adding calcium thiocyanate to an excess of potassium amide. In appearance and general properties it closely resembles the analogous barium and strontium compounds.

**Potassium Ammonosodiate**,  $\text{NaNK}_2.2\text{NH}_3$  or  $\text{NaNH}_2.2\text{KNH}_2$ .<sup>22</sup> The first formula represents this compound as potassium ammonosodiate with two molecules of ammonia of crystallization, the sec-

<sup>20</sup> Franklin, *J. Phys. Chem.*, **16**, 682 (1912).

<sup>21</sup> Franklin, *J. Am. Chem. Soc.*, **37**, 2205 (1915).

<sup>22</sup> Franklin, *J. Phys. Chem.*, **23**, 36 (1919).

ond as a molecular compound of sodium amide and potassium amide.

This compound has been obtained by the action of potassium amide, in solution in liquid ammonia, on the slightly soluble sodium amide. The reaction involved may be represented by the equation,  $\text{NaNH}_2 + 2\text{KNH}_2 = \text{NaNK}_2 + 2\text{NH}_3$ , or simply,  $\text{NaNH}_2 + 2\text{KNH}_2 = \text{NaNH}_2 \cdot 2\text{KNH}_2$ , which of course leaves the question of the constitution of the compound quite unanswered, though it is not unreasonable to say that the stronger base acts on the weaker, and therefore amphoteric, base to form a potassium sodiate.

Potassium ammonosodiate has also been obtained as a crystalline precipitate by adding sodium iodide to an excess of potassium amide in solution in liquid ammonia, and by allowing a solution containing metallic sodium and potassium amide, the latter in excess, to stand in contact with a small spiral of iron wire. The salt which may be obtained well crystallized, does not lose ammonia at  $100^\circ$  in vacuum. At higher temperatures it melts, loses ammonia and attacks the glass container. The compound is decomposed by liquid ammonia solutions of acids with the formation of salts of sodium and potassium. For example, the action of ammonium nitrate is represented by the equation,  $\text{NaNK}_2 \cdot 2\text{NH}_3 + 3\text{NH}_4\text{NO}_3 = \text{NaNO}_3 + 2\text{KNO}_3 + 6\text{NH}_3$ . Potassium ammonosodiate is distinctly more soluble than sodium amide and much less soluble than potassium amide.

**Potassium Ammonolithiate,  $\text{LiNK}_2 \cdot 2\text{NH}_3$ .** Pure specimens of this salt have been obtained in the form of minute, colorless, very slightly soluble crystals by adding lithium iodide to an excess of potassium amide and also by allowing metallic lithium with potassium amide in excess to stand for a time in the presence of a minute quantity of platinum black. Lithium amide, formed in the one case by the action of potassium amide on lithium iodide, in the other by the action of metallic lithium on ammonia, unites with potassium amide present in excess to form potassium ammonolithiate. The salt dissolves in liquid ammonia solutions of ammonium iodide forming iodides of potassium, lithium and ammonium.

**Mono-Rubidium Ammonosodiate,  $\text{NaNHRb} \cdot \text{NH}_3$ .** This compound has been obtained by dissolving sodium amide in a solution of rubidium amide and also by allowing a solution of the two metals to stand in contact with a very small quantity of platinum black until the blue color of the solution disappears. By properly concentrating the solutions obtained by these procedures the compound is deposited well crystallized. Excepting that it is much more soluble this salt resembles potassium ammonosodiate in general appearance and behavior.

In view of the observations recorded in the preceding pages to the effect that potassium amide forms compounds with the amides

of practically all less positive metals including the amides of sodium and lithium it was surmised that possibly the amide of the still more positive rubidium acting as an ammono base might react with potassium amide to form an ammonopotassiate of rubidium. However attempts to crystallize a definite compound from solutions containing rubidium amide and potassium amide were unsuccessful. The two amides separate as isomorphous mixtures varying in composition with the composition of the liquid phase.

**Di-Rubidium Ammonosodiate**,  $\text{NaNRb}_2\cdot 2\text{NH}_3$ . From the solution formed by dissolving sodium amide in an excess of rubidium amide a very soluble compound of the composition represented by the above formula separates well crystallized from highly concentrated solutions.

**Mono-Rubidium Ammonolithiate**,  $\text{LiNHRb}\cdot\text{NH}_3$ . A specimen of this compound has been prepared by the action of a solution of rubidium amide on metallic lithium in the presence of platinum black after the manner described for the preparation of potassium ammonolithiate. Rubidium ammonolithiate is very slightly soluble in liquid ammonia.

**Potassium Ammonoceriate**,  $\text{Ce}(\text{NHK})_3\cdot x\text{NH}_3$ , and **Potassium Ammonolanthanate**,  $\text{La}(\text{NHK})_3\cdot x\text{NH}_3$ .<sup>23</sup> The first of these compounds has been prepared by the action of a solution of potassium amide in excess on metallic cerium and on cerium iodide, the other in a similar manner from metallic lanthanum and from lanthanum iodide. Both compounds are obtained in the form of precipitates containing from 2.5 to 3 molecules of ammonia.

**Potassium Ammonogalliate**,  $\text{KNGaNHK}\cdot 3\text{NH}_3$ .<sup>24</sup> Bergstrom prepared an extremely soluble salt of the composition represented by the above formula by the action of potassium amide on metallic gallium and has also found that a sodium ammonogalliate probably exists.

<sup>23</sup> Bergstrom, *J. Am. Chem. Soc.*, 47, 1836 (1925).

<sup>24</sup> Unpublished observations.

## CHAPTER VIII.

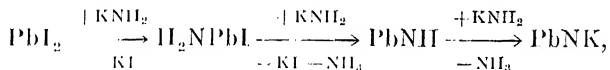
### AMMONOBASIC SALTS.

Salts of many of the heavy metals when brought into contact with liquid ammonia undergo ammonolytic decomposition in a manner entirely analogous to the familiar hydrolytic decomposition brought about by the action of water. Liquid ammonia ammonolyzes the normal salts to ammonobasic salts, liquid water hydrolyzes them to aquobasic salts.

**Ammonobasic Lead Iodide**,  $\text{Pb-N-Pb-I.2NH}_3$ ,  $\text{Pb-N-Pb-I.NH}_3$ .<sup>1</sup> These compounds may just as well be represented by other formulas including respectively,  $\text{Pb}_3\text{N}_2.\text{PbI}_2.4\text{NH}_3$  and  $\text{Pb}_3\text{N}_2.\text{PbI}_2.2\text{NH}_3$ .

Lead iodide dissolves abundantly in liquid ammonia forming a cloudy solution from which a small amount of a white precipitate of the composition represented by the first formula above slowly separates.

When potassium amide is added in successive small portions to a lead iodide solution the normal salt is converted first into the insoluble ammonobasic salt, thence into lead imide which is likewise insoluble, and finally into the very soluble potassium ammonoplumbite. The reactions involved are represented by the scheme,



in which the simpler formula,  $\text{H}_2\text{NPbI}$ , instead of the more complex one given above is used to represent the ammonobasic salt. On heating this white basic salt in vacuum to 200° it is converted into a brown product of the composition represented by the second of the above formulas.

This successive formation of ammonobasic lead iodide, lead imide and potassium ammonoplumbite and the reverse conversion of potassium ammonoplumbite, first into lead imide, thence into ammonobasic lead iodide and finally into lead iodide lend themselves readily to an instructive lecture experiment.

The legs A and C of the three-legged reaction tube shown in Figure 4 (see p. 33) contain, respectively, liquid ammonia solutions of ammonium iodide and potassium amide. Leg B contains a small quantity of dilute solution of lead

<sup>1</sup> Franklin, *J. Am. Chem. Soc.*, 27, 845 (1905).



iodide. On pouring a few drops of potassium amide solution carefully on to the surface of the solution of the lead iodide a precipitate is formed, the under portions of which are white, the upper portions brick red. The white part of the precipitate is the ammonobasic salt, the colored part is lead imide. When the tube is then shaken the lead imide, in the presence of lead iodide solution, is converted into the pure white basic salt which settles to the bottom of leg *B*. Further careful additions of potassium amide, accompanied by thorough mixing of the contents of leg *B* gradually precipitates all the lead in the form of the colorless basic salt containing no admixture of lead imide. Continued addition of small portions of potassium amide solution, care being taken to keep the contents of leg *B* well agitated, brings about the gradual conversion of the pure white basic salt, through mixtures containing both the basic salt and lead imide, finally, to the pure brick red imide. Further additions of potassium amide then dissolves the imide to a colorless solution of potassium ammonoplumbite. The reverse process may now be brought about by pouring successive small portions of the hydriodic acid (ammonium iodide) solution from leg *A* into the solution of potassium ammonoplumbite. Following the neutralization of excess of the potassium base a precipitate of lead imide appears. After all the lead is precipitated in the form of the imide, further additions of the acid gradually transforms the lead imide into the basic salt, which in turn finally dissolves to form a clear, colorless solution of lead iodide. With considerable quantities of ammonium iodide and potassium amide in legs *A* and *C*, and a small quantity of lead solution in *B*, the procedure thus described may be repeated until the ammonium iodide and potassium amide are exhausted. Obviously potassium iodide resulting from the action of hydriodic acid on potassium amide accumulates in *B*.

**Ammonobasic Lead Nitrate,**<sup>2</sup>  $\text{H}_2\text{N-Pb-NH-Pb-NO}_3$ . Lead nitrate dissolves readily in liquid ammonia but not to form a clear solution. A small portion of the salt is ammonolyzed to a colorless, insoluble, ammonobasic lead nitrate, which gradually settles from the solution, and after the lapse of sufficient time becomes crystalline. Addition of potassium amide increases the amount of the basic salt, addition of ammonium nitrate dissolves it. The precipitated basic product was found to have a composition approximating that represented by the above formula.

**Ammonobasic Aluminum Iodides,**  $\text{AlI}_{3.3}\text{Al}(\text{NH}_2)_3.6\text{NH}_3$ ,  $\text{Al}(\text{NH}_2)_2\text{I}.\text{Al}(\text{NH}_2)_3.\text{NH}_3$  and  $\text{Al}(\text{NH})\text{I}.\text{Al}(\text{NH}_2)_3$ .<sup>3</sup> A soluble ammonobasic iodide of aluminum the composition of which is represented by the first of the above formulas has been obtained by adding somewhat less than one and a half molecular equivalents of potassium amide to a liquid ammonia solution containing one molecular equivalent of the very soluble aluminum iodide and evaporating to crystallization, at laboratory temperature, the solution of the basic salt thus formed. The crystallized salt does not lose its ammonia of crystallization when heated in vacuum at  $165^\circ$ . When this basic salt is crystallized from solution at  $-33^\circ$  it retains not less than eighteen molecules of ammonia.

<sup>2</sup> Franklin, *J. Am. Chem. Soc.*, 27, 846 (1905).

<sup>3</sup> Franklin, *J. Am. Chem. Soc.*, 37, 847 (1913).

When potassium amide is added to a solution of this soluble basic salt a bulky, amorphous precipitate of an insoluble ammonobasic aluminum iodide represented by the second formula is formed. On heating this compound in vacuum to  $160^{\circ}$  it loses two molecules of ammonia to yield a product of the composition represented by the third formula.

**Ammonobasic Beryllium Chloride.**<sup>4</sup> A solution of ammonium chloride in liquid ammonia dissolves metallic beryllium with the evolution of hydrogen to form normal beryllium chloride, which separates well crystallized from cold concentrated solutions with four molecules of ammonia,  $\text{BeCl}_2 \cdot 4\text{NH}_3$ . The solution of the normal salt further reacts with the metal yielding a slightly soluble ammonobasic salt approximately of the composition represented by the formula,  $\text{BeCl}_2 \cdot \text{Be}(\text{NH}_2)_2 \cdot x\text{NH}_3$ .

**Ammonobasic Beryllium Bromides,**  $2\text{BeBr}_2 \cdot \text{Be}(\text{NH}_2)_2 \cdot 8\text{NH}_3$ ,  $\text{BeBr}_2 \cdot 3\text{Be}(\text{NH}_2)_2 \cdot 8\text{NH}_3$  and  $\text{BeBr}_2 \cdot 3\text{Be}(\text{NH}_2)_2 \cdot 4\text{NH}_3$ . By dissolving metallic beryllium in a liquid ammonia solution containing one-half the amount of ammonium bromide required to satisfy the equation,  $\text{Be} + 2\text{NH}_4\text{Br} = \text{BeBr}_2 + 2\text{NH}_3 + \text{H}_2$ , Bergstrom obtained a solution from which he isolated two ammonobasic salts. The one represented by the first of the above formulas is very soluble, the other represented by the second formula is slightly soluble. This latter salt separates from solution with eight molecules of ammonia of crystallization, four of which it loses in vacuum at  $20^{\circ}$ .

**Ammonobasic Beryllium Iodides,**  $\text{BeI}_2 \cdot 3\text{Be}(\text{NH}_2)_2 \cdot 4\text{NH}_3$  and  $\text{BeI}_2 \cdot 5\text{Be}(\text{NH}_2)_2 \cdot 4\text{NH}_3$ . By the action of a liquid ammonia solution of ammonium iodide on an excess of metallic beryllium Bergstrom obtained two very soluble crystalline ammonobasic salts represented respectively by the above formulas, and an amorphous, insoluble basic product of unknown composition.

**Ammonobasic Molybdenum Chloride,**  $\text{Mo}(\text{NH}_2)_3 \cdot \text{MoCl}_3 \cdot 10\text{NH}_3$ ,  $\text{Mo}(\text{NH}_2)_3 \cdot \text{MoCl}_3$ .<sup>5</sup> The ammonated ammonobasic salt was obtained as a brown powder by the action of liquid ammonia on insoluble molybdenum trichloride. Exposed to the air it rapidly loses ammonia to form the ammonia-free compound.

**Ammonobasic Auric Chlorides.** Two compounds of the respective formulas,  $\text{Au}(\text{NH}_2)_2 \cdot \text{Cl}$  and  $\text{HN}[\text{Au}(\text{NH}_2)\text{Cl}]_2$ , which were prepared by Weitz<sup>6</sup> by the action of aqua ammonia on gold chloride, are to be looked upon as ammonobasic auric chlorides.

**Ammonobasic Mercuric Chloride,**  $\text{H}_2\text{N} \cdot \text{Hg} \cdot \text{Cl}$ .<sup>7</sup> When mercuric

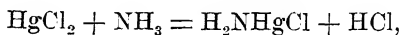
<sup>4</sup> Bergstrom, *J. Am. Chem. Soc.*, **50**, 657 (1928).

<sup>5</sup> Rosenheim and Braun, *Z. anorg. Chem.*, **46**, 311 (1905).

<sup>6</sup> Weitz, *Ann. Chem.*, **410**, 117 (1915).

<sup>7</sup> Franklin and Kraus, *Am. Chem. J.*, **23**, 299 (1900); Franklin, *J. Am. Chem. Soc.*, **27**, 841 (1905).

chloride and liquid ammonia are brought together a two-liquid phase system comes into existence, a less dense phase consisting of a dilute solution of mercuric chloride in liquid ammonia, and a denser one of the composition represented approximately by the formula,  $\text{HgCl}_2 \cdot 12\text{NH}_3$ . At the same time a portion of the salt undergoes ammonolysis in accordance with the equation,



to form an ammonobasic mercuric chloride which with the lapse of time becomes crystalline. This basic salt is identical with the long-known infusible white precipitate.

**Ammonobasic Mercuric Bromide,  $\text{Hg}^{\cdot}\text{N}\text{-Hg-Br}$ .**<sup>8</sup> A dense, yellow residue of this ammonobasic salt is left behind when mercuric bromide is dissolved in liquid ammonia whereas in the presence of a minute amount of ammonium bromide the salt dissolves completely to a clear, colorless solution. Successive careful additions of potassium amide to this solution precipitates the ammonobasic salt,  $2\text{HgBr}_2 + \text{NH}_3 = \text{Hg}^{\cdot}\text{N}\text{-Hg-Br} + 3\text{HBr}$ , which, in turn, by the further addition of the ammono base, is converted into mercuric nitride.

**Ammonobasic Mercuric Iodide,  $\text{Hg}^{\cdot}\text{N}\text{-Hg-I}$ .** Mercuric iodide, in the presence of small amounts of ammonium iodide, dissolves abundantly in liquid ammonia to form a clear, colorless solution from which, with proper adjustment of concentration and temperature, the diammonated salt separates beautifully crystallized. On exposure to the atmosphere these colorless crystals gradually lose their ammonia of crystallization, thus efflorescing to the red anammonous mercuric iodide. Addition of potassium amide to the liquid ammonia solution of mercuric iodide precipitates the ammonobasic iodide which in turn on treatment with excess of potassium amide is converted into mercuric nitride.

**Ammonobasic Mixtures.**<sup>9</sup> A considerable number of metallic salts, including stannic iodide, zirconium iodide and certain halogen salts of tungsten, molybdenum, antimony and uranium, when brought into contact with liquid ammonia, have been found to undergo ammonolysis to form ammonobasic mixtures of indefinite composition.

The observations of Fitzgerald on the behavior of stannic iodide in liquid ammonia are especially interesting in this connection.

<sup>8</sup> Fitzgerald, *J. Am. Chem. Soc.*, **29**, 660 (1907).

<sup>9</sup> Stähler and Denk, *Ber.*, **38**, 2611 (1905); Franklin, *J. Am. Chem. Soc.*, **27**, 849 (1908), **29**, 35 (1907); *Am. Chem. J.*, **47**, 312, 361 (1912); Fitzgerald, *J. Am. Chem. Soc.*, **29**, 1695 (1907); Garret, Thesis, Stanford University, 1921; Bergstrom, *J. Am. Chem. Soc.*, **47**, 2317 (1925).

When a small quantity of liquid ammonia is poured from the one leg of a two-legged reaction tube (Fig. 3, p. 25) upon a few crystals of stannic iodide contained in the second leg, the salt, in the presence of a small quantity of ammonium iodide, dissolves to a dense, colorless, clear solution. When liquid ammonia is carefully poured upon the surface of this solution the separation of a white precipitate is observed occupying a zone between the concentrated solution of stannic iodide and the specifically lighter liquid ammonia. On shaking the tube, thus mixing its contents, the precipitate disappears. Again pouring liquid ammonia upon the surface of the solution the precipitate reappears to disappear again on shaking. The separation of the precipitate may be observed several times by repeating the operations thus described. After a relatively large amount of liquid ammonia has been added the precipitate becomes permanent and the separation of tin from the solution is complete as is shown by the observation that the addition of potassium amide to the supernatant solution fails to produce any further precipitate. Distilling the solvent from the precipitate into the first leg of the reaction tube, thereby concentrating the solution of hydriodic acid (ammonium iodide), brings about the conversion of the ammonobasic tin iodide into the normal salt. Analyses of the precipitate showed it to be an ammonobasic mixture of indefinite composition.

## CHAPTER IX.

### MERCURY NITROGEN COMPOUNDS.

By the action of aqua ammonia on mercuric oxide and on mercuric salts a large number of products has been obtained concerning the nature of which widely divergent opinions have been expressed.<sup>1</sup>

According to the view of Rammelsberg, which in more recent years has been stoutly supported by Pesci, all the mercury ammonia compounds are assumed to be derivatives of so-called dimercuriammonium hydroxide,  $\text{Hg}_2\text{NOH}$ , or in other words, of ammonium hydroxide in which the four ammonium hydrogen atoms are replaced by two atoms of mercury. According to Pesci dimercuriammonium hydroxide and its salts are prone to the formation of hydrates and to union with ammonium and mercuric salts to form a large variety of double and complex salts. Thus Millon's base is assumed to be hydrated dimercuriammonium hydroxide,  $\text{Hg}_2\text{NOH}\cdot x\text{H}_2\text{O}$ ; the so-called chloride of Millon's base, a hydrated dimercuriammonium chloride,  $\text{Hg}_2\text{NCl}\cdot x\text{H}_2\text{O}$ ; Nessler's precipitate, a hydrated dimercuriammonium iodide,  $\text{Hg}_2\text{NI}\cdot x\text{H}_2\text{O}$ ; the ammonated salt,  $\text{HgCl}_2\cdot\text{NH}_3$ , a triple salt of dimercuriammonium chloride, ammonium chloride and mercuric chloride,  $\text{Hg}_2\text{NCl}\cdot 3\text{NH}_4\text{Cl}\cdot 2\text{HgCl}_2$ . Furthermore Pesci sought to show that the familiar fusible and infusible white precipitates, two compounds represented most simply by the formulas,  $\text{HgCl}_2\cdot 2\text{NH}_3$  and  $\text{H}_2\text{NHgCl}$ , are double salts of dimercuriammonium chloride and ammonium chloride as represented by the respective formulas,  $\text{Hg}_2\text{NCl}\cdot 3\text{NH}_4\text{Cl}$  and  $\text{Hg}_2\text{NCl}\cdot \text{NH}_4\text{Cl}$ , while Rây, following Pesci,<sup>2</sup> went so far as to represent the double salt of mercuric chloride and ammonium chloride,  $2\text{HgCl}_2\cdot \text{NH}_4\text{Cl}$ , as a hydrochloric acid addition product of dimercuriammonium chloride,  $\text{Hg}_2\text{NCl}\cdot 4\text{HCl}$ .<sup>3</sup>

<sup>1</sup> Pesci, *Gazz. Chim. ital.*, **19**, 509 (1889), **20**, 485 (1890), *Z. anorg. Chem.*, **21**, 361 (1899); Hofmann and Marburg, *Ann. Chem.*, **305**, 191 (1899); *Z. anorg. Chem.*, **23**, 126 (1899); Furth, *Monatsh.*, **23**, 1147 (1902); François, *Compt. rend.*, **130**, 332, 1022 (1900); Strömholm, *Z. anorg. Chem.*, **57**, 72 (1908); Widman, *Z. anorg. Chem.*, **68**, 1 (1910); Gaudechon, *Ann. Chim.*, [8] **22**, 145 (1911); Franklin, *J. Am. Chem. Soc.*, **27**, 827 (1905), **29**, 35 (1907), *Am. Chem. J.*, **47**, 361 (1912).

<sup>2</sup> Rây, *Proc. Chem. Soc.*, **17**, 96 (1901); Dammer, *Handb. anorg. Chem.*, **4**, 630 (1913); Moissan, *Traité chim. min.*, **5**, 404 (1906).

<sup>3</sup> If following the Rammelsberg-Pesci theory the compound  $\text{HgCl}_2\cdot 2\text{NH}_3$ , be formulated as a double salt of dimercuriammonium chloride and ammonium chloride,  $\text{Hg}_2\text{NCl}\cdot 3\text{NH}_4\text{Cl}$ , then there appears to be no good reason why such a compound as  $\text{AgI}\cdot \text{NH}_3$ , for example, should not be a double salt of tetrargenti-

Others,<sup>4</sup> assuming the existence of several types of compounds, formulate the fusible white precipitate as mercuridiammonium chloride,  $\text{Hg}(\text{NH}_3\text{Cl})_2$ , ammonium chloride in which a mercury atom takes the place of one hydrogen atom in each of two molecules of the salt; the infusible white precipitate as ammonium chloride in which two ammonium hydrogen atoms are replaced by a mercury atom,  $\text{HgNH}_2\text{Cl}$ ; and the chloride of Millon's base as oxydimercuri-ammonium chloride,  $(\text{HgOHg})\text{NH}_2\text{Cl}$ . This formula represents a molecule of ammonium chloride in which the  $\text{HgOHg}$  group takes the place of two hydrogen atoms.

According to still other writers the fusible and infusible precipitates are removed from the category of substituted ammonium salts and formulated respectively as ammonated mercuric chloride,  $\text{HgCl}_2 \cdot 2\text{NH}_3$ , and amido mercuric chloride,  $\text{H}_2\text{NHgCl}$ , leaving the salts of Millon's base and related compounds to be formulated in accordance with the assumption that they are substituted ammonium salts.

Now the Hofmann-Rammelsberg-Pesci theory concerning the nature of the mercuriammonium compounds is all but certainly erroneous. (Cf., however, footnote 8.) In the writer's opinion they are without adequate foundation in experimental fact and should be replaced by a modified and extended form of Kane's amide theory.

Long ago Robert Kane<sup>5</sup> clearly recognized the true nature of the mercury nitrogen compounds when he pointed out the facts, first, that the fusible white precipitate,  $\text{HgCl}_2 \cdot 2\text{NH}_3$ , is one of the many known compounds in which ammonia plays a part analogous to that played by water in salts containing water of crystallization, second, that the infusible white precipitate,  $\text{H}_2\text{NHgCl}$ , is a compound related to ammonia as the ordinary basic salts are related to water and third, that the yellow, insoluble compounds, later to become known as salts of Millon's base and as hydrated salts of dimercuri-ammonium, are products resembling the ordinary basic salts.

In agreement with Kane's views the writer has shown that all monium iodide and ammonium iodide and given the formula,  $\text{Ag}_3\text{NI} \cdot 3\text{NH}_4\text{I}$ , or why even the hydrated barium chloride,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ , should not be regarded as a double salt of a barium oxonium chloride and oxonium chloride and given the formula,  $\text{Ba}_3\text{O}_2\text{Cl}_2 \cdot 4\text{OH}_2\text{Cl}$ . It is certainly just as reasonable so to formulate these solvated salts as it is to follow Pesci and represent ammonated mercuric iodide,  $\text{HgI}_2 \cdot 2\text{NH}_3$ , which, as noted above, effloresces on exposure at laboratory temperatures, as a double salt of dimercuri-ammonium iodide and ammonium iodide,  $\text{Hg}_2\text{NI} \cdot 3\text{NH}_4\text{I}$ .

<sup>4</sup> Gmelin-Kraut, *Handb. anorg. Chem.*, 3, 818, 840 (1875); Watts, *Dict. Chem.*, 3, 206 (1892); Ladenburg, *Handwörterb. Chem.*, 10, 148 (1892); Abegg, *Handb. anorg. Chem.*, 2, II, 866 (1905); Mellor, *Treatise Inorg. and Theoret. Chem.*, 4, 784, 999 (1923).

<sup>5</sup> Kane, *Ann. chim. phys.*, 72, 337 (1839), "Elements of Chemistry," Am. Ed., 1843, p. 300.

the mercury ammonium compounds may be regarded as members of three general classes of compounds as follows: 1, Normal mercuric salts with ammonia of crystallization, 2, ammonobasic mercuric salts and 3, mixed aquobasic-ammonobasic mercuric salts. A possible fourth class includes so-called Millon's base,  $\text{Hg}_2\text{NOH}\cdot x\text{H}_2\text{O}$ , and its dehydration products which may be looked upon as mixed aquo-ammono bases formed by the dehydration of an hypothetical mercuric hydroxide amide,  $\text{HOHgNH}_2$ . It seems questionable however whether any of these reported products exist as definite chemical compounds.

1. **Mercuric Salts with Ammonia of Crystallization.** Conspicuous among the properties held in common by water and ammonia is the ability of each to form addition products with a long list of metallic salts; water to form compounds known as salt hydrates or salts with water of crystallization, ammonia to form analogous compounds which may be called salt ammonates or salts with ammonia of crystallization.<sup>6</sup>

The ammonated mercuric salts represented by the formulas,  $\text{HgCl}_2\cdot 2\text{NH}_3$ ,  $\text{HgBr}_2\cdot 2\text{NH}_3$ ,  $\text{HgI}_2\cdot 2\text{NH}_3$ , are formed by the action of ammonia, either in the gaseous or liquid state or in solution in water, on the respective mercuric salts provided that in the liquid ammonia or aqua ammonia solutions the appropriate acid (ammonium salt) is present in sufficient concentration to prevent ammonolytic decomposition of the normal mercuric salt. Like most hydrated salts these ammonated mercuric salts show an appreciable vapor tension. The crystals of ammonated mercuric iodide, for example, on exposure to the atmosphere exhibit the phenomenon of efflorescence in that the colorless crystals lose ammonia and disintegrate to the red anammonous salt.

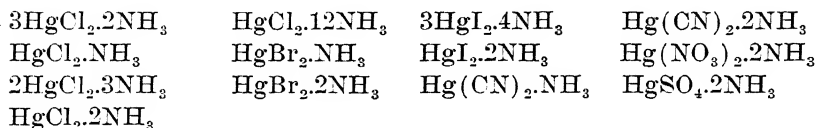
"Excepting that the combination of ammonia with salts, like that of water, must be due to coordination"<sup>7</sup> no attempt is made to explain the nature of the fusible white precipitate and other compounds formed by the addition of ammonia to mercuric salts

<sup>6</sup> A great many salts form addition products with ammonia as well as with water, calcium chloride for example forms a hexahydrate,  $\text{CaCl}_2\cdot 6\text{H}_2\text{O}$ , and an octammonate,  $\text{CaCl}_2\cdot 8\text{NH}_3$ . Some salts form addition products simultaneously with water and ammonia. A copper sulfate hydrate-ammonate represented by the formula,  $\text{CuSO}_4\cdot 4\text{NH}_3\cdot \text{H}_2\text{O}$ , is known. Certain others conspicuous for their tendency to form hydrates do not form ammonates. Sodium carbonate and sulfate, for example, apparently do not form ammonates, while the halides of silver, lead and mercury form addition products with ammonia but not with water. Others, which form both hydrates and ammonates when given, so to speak, their choice by crystallizing them from a mixture of the two solvents, namely from aqua ammonia, are found separating now as hydrates and then as ammonates. Calcium nitrate for example separates from aqua ammonia solution with water of crystallization, cupric nitrate with ammonia of crystallization.

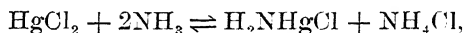
<sup>7</sup> Sidgwick, "The Electronic Theory of Valence," p. 200 (1927).

further than to have thus shown that they are to be looked upon as members of the large class of solvated salts.<sup>8</sup>

Ammonated mercuric salts have been reported as follows,<sup>9</sup>



2. **Ammonobasic Mercuric Salts.** As has been shown in another place (*cf.* Chapter VIII, p. 77) mercuric chloride under the action of liquid ammonia undergoes ammonolytic decomposition in accordance with the reversible equation,



to form an ammonobasic mercuric chloride.

It happens that most ammonobasic salts, other than those of mercury, are hydrolyzed in the presence of water, from which circumstance it follows that such compounds can be prepared only when liquid ammonia is used as solvent in which to carry out the necessary reactions, or in any event when the solvent used is other than water. The ammonobasic salts of mercury are conspicuous exceptions to the rule. Ammonobasic mercuric chloride is capable of existence in the presence of water and is therefore formed by the action of ammonia on mercuric chloride whether water is present or not.

When ammonia is added to a water solution of mercuric chloride a precipitate of ammonated mercuric chloride,  $\text{HgCl}_2 \cdot 2\text{NH}_3$ , is formed provided ammonium chloride, which functions as an acid, is present in sufficient concentration to prevent the ammonolytic decomposition of the salt. Lowering the concentration of the acid (ammonium chloride) below something like half normal, either by adding potassium hydroxide or by diluting the solution, results in the gradual conversion of the ammonated salt into the ammonobasic salt in accordance with the equation given above to represent the

<sup>8</sup> If the fusible white precipitate and, for example dihydrated cupric chloride, be written as coordination compounds,  $\text{Hg}[\text{NH}_3]_2\text{Cl}_2$  and  $\text{Cu}[\text{OH}_2]_2\text{Cl}_2$ , it follows of course that the first formula may, in a way, be said to represent a mercury-substituted ammonium chloride; the second represents two molecules of oxonium chloride in each of which a hydrogen atom is replaced by a divalent copper atom. Hofmann, Hartmann and Nagel [*Ber.*, 58, 808 (1925)] state that ammonium chloride acting as an acid reacts with metallic copper at elevated temperatures in accordance with the equation,  $\text{NH}_4\text{Cl} + \text{Cu} = (\text{CuNH}_3)\text{Cl} + \text{H}$ , to form a salt which is to be looked upon as ammonium chloride in which one of the hydrogen atoms is replaced by an atom of copper.

<sup>9</sup> Franklin, *J. Am. Chem. Soc.*, 29, 35 (1907); Holmes, *J. Chem. Soc.*, 113, 74 (1918).



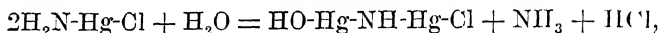
ammonolytic decomposition of mercuric chloride in liquid ammonia. Inversely, in water as in liquid ammonia, the basic salt is converted into the normal salt when the concentration of the ammonium chloride solution is made sufficiently high.

Insoluble ammonobasic products, represented by the following formulas, are recorded in the literature as mercuriammonium compounds.

$\text{Hg}_2\text{N}_3\text{H}_8\text{Cl}_3$	$\text{HgNH}_2\text{Br}$	$\text{Hg}_2\text{NI}$
$\text{HgNH}_2\text{Cl}$	$\text{Hg}_2\text{NBr}$	$\text{Hg}_9\text{N}_4\text{I}_6$
$\text{Hg}_2\text{NCl}$	$\text{Hg}_2\text{NHBr}_2$	$\text{HgNH}_2\text{F}$
$\text{Hg}_2\text{NHCl}_2$	$\text{Hg}_5\text{N}_2\text{Br}_4$	$\text{HgNH}_2\text{NO}_3$
$\text{Hg}_2\text{NH}_2\text{Cl}_3$	$\text{Hg}_8\text{N}_9\text{H}_{20}\text{Br}_9$	$\text{Hg}_2\text{NNO}_3$
$\text{Hg}_2\text{NH}_4\text{Cl}_5$	$\text{Hg}_9\text{N}_4\text{Br}_6$	$\text{Hg}_2\text{NNO}_2$
$\text{Hg}_5\text{N}_2\text{Cl}_4$	$\text{HgNH}_2\text{I}$	$\text{Hg}_2\text{N}(\text{C}_2\text{H}_4\text{O}_2)$

It is highly probable that some of these products are ammonobasic mixtures and not definite chemical compounds.

3. **Mixed Aquobasic Ammonobasic Mercuric Salts.** When the practically insoluble ammonobasic salt,  $\text{H}_2\text{NHgCl}$ , is washed with water or aqua ammonia it is slowly converted into a yellowish, insoluble product which has long been known as the chloride of Millon's base. The most reasonable interpretation of the reaction involved, which may be represented by the equation,



is to the effect that by the action of water the ammonobasic mercuric salt is hydrolyzed to a mixed aquobasic ammonobasic salt.<sup>10</sup>

The properties and chemical behavior of the chloride of Millon's base support the view that it belongs to the class of basic salts. Like most basic salts it is insoluble and noncrystalline or at best microcrystalline. It is converted into the ammonated mercuric chloride,  $\text{HgCl}_2 \cdot 2\text{NH}_3$ , by digestion with ammonium chloride solution just as aquobasic salts are converted into normal salts by the action of aqueous acids, and is hydrolyzed to mercuric oxide by long-continued washing with water or with potassium hydroxide solution.

Applying the principles of the Phase Rule, as suggested by Miller and Kendrick,<sup>11</sup> Stromholm, Widman, and Gaudechon have con-

<sup>10</sup> One does not get very far in writing structural formulas for basic salts. Instead of the above formula one may just as well write,  $\text{H}_2\text{NHgOHgCl}$ ,  $\text{HgO.H}_2\text{NHgCl}$ ,  $\text{HgCl}_2 \cdot \text{Hg}_3\text{N}_2 \cdot 2\text{H}_2\text{O}$ ,  $3\text{HgCl}_2 \cdot \text{Hg}_3\text{N}_2 \cdot 6\text{HgO} \cdot 4\text{NH}_3$ , or any one of a considerable number of other possible formulas.

<sup>11</sup> Miller and Kendrick, *J. Phys. Chem.*, **7**, 259 (1903).

firmed the existence of the compound represented by the formula,  $\text{HOHgNHHgCl}$ , while at the same time their work eliminates some fourteen products, formed in various ways by the interaction of ammonia and mercuric chloride, from the list of known compounds.

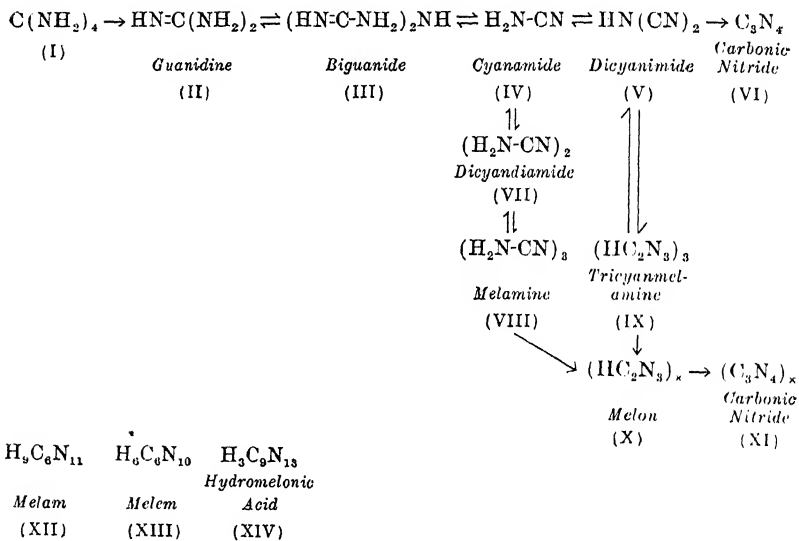
Finally some forty or more products formed by the action of ammonia on mercuric salts other than mercuric chloride have been reported as mercuriammonium compounds some of which <sup>12</sup> are probably aquobasic ammonobasic salts of definite composition while others are certainly basic mixtures.

<sup>12</sup> Franklin, *J. Am. Chem. Soc.*, 29, 35 (1907).

## CHAPTER X.

### AMMONO CARBONIC ACIDS.

The formula,  $C(NH_2)_4$ , represents the unknown nitrogen analog of ortho carbonic acid. Assuming such a compound to lose ammonia stepwise as represented by the top horizontal rows in the scheme,



it becomes obvious that guanidine, biguanide, cyanamide, and dicyanimide are to be looked upon as ammono carbonic acids. Furthermore dicyandiamide, melamine, tricyanmelamine, melon, melam, melem and hydromelonic acid are ammono carbonic acids while the formulas (VI) and (XI) represent respectively monomolecular and polymolecular carbonic anammonides. Melon, a highly polymerized form of dicyanimide, is insoluble and infusible and is not known to form metallic salts. It is formed by heating any one of the ammono carbonic acids. Melam and melem are noncrystalline, insoluble products of rather uncertain chemical individuality.

Excepting that ortho-ammono carbonic acid and monomolecular carbonic nitride are unknown and that melon has not been converted into polymeric carbonic nitride all the transformations indicated in the table have been accomplished.

**Nomenclature.** Following a procedure sometimes made use of in naming the numerous silicic acids and other complex acids we shall find it convenient to speak of the ammono carbonic acids containing one carbon atom in the molecule as ammono unicarbonic acids, those containing two atoms as ammono dicarbonic acids, those containing three as ammono tricarbonic acids and so forth. Accordingly guanidine and cyanamide are unicarbonic acids, biguanide, dicyanimide and dicyandiamide are dicarbonic acids. Melamine and tricyanmelamine are cyclic compounds. The one containing three carbon atoms in the molecule is a cyclic ammono tricarbonic acid, the other containing six is a cyclic ammono hexacarbonic acid. Hydromelonic acid,  $H_3C_9N_{13}$ ,  $(C_3N_4)_3 \cdot NH_3$  is a nonocarbonic acid.

**Acid Properties of the Ammono Carbonic Acids.** Of the compounds listed in the table above dicyanimide, tricyanmelamine and hydromelonic acid are strong acids. In water solution dicyanimide and tricyanmelamine sharply redden litmus, dissolve alkali metal carbonates with the evolution of carbon dioxide, and conduct the electric current with a facility approaching that of the strong mineral acids.<sup>1</sup>

According to Liebig<sup>2</sup> hydromelonic acid in water solution has a sour taste and reacts strongly acid while its potassium salt in water solution shows a neutral reaction. No one of these compounds forms salts by addition of hydrochloric acid.

Aqueous solutions of cyanamide and dicyandiamide are neutral in reaction. The former forms an unstable hydrochloride, the latter does not form a hydrochloride. Metallic derivatives of both compounds are known which, excepting certain insoluble heavy metal salts, are highly hydrolyzed in the presence of water.

Melamine, biguanide and guanidine show not the slightest acid properties in water solution. On the contrary melamine behaves as a weak base, biguanide and guanidine as strong bases. That is to say these compounds are bases in the same sense that ammonia is a base in that they unite with acids to form salts and dissolve in water to give alkaline solutions.

Certainly in respect to their behavior in water solution dicyanimide, tricyanmelamine and hydromelonic acid are strong acids, cyanamide and dicyandiamide are at best extremely weak acids while biguanide and guanidine show no acid properties whatsoever.

In liquid ammonia solution on the other hand all these com-

<sup>1</sup> Madelung and Kern, *Ann. Chem.*, **427**, 1 (1922).

<sup>2</sup> Liebig, *Ann. Chem.*, **95**, 257 (1855).

pounds<sup>3</sup> behave as acids, guanidine the weakest acid among them, to the extent at least that it attacks metallic potassium with the evolution of hydrogen and reacts with potassium amide to form a dipotassium salt.

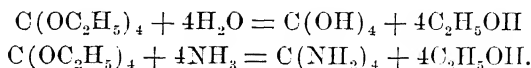
Since our knowledge concerning acids and bases has been developed largely in connection with the study of water solutions we have come, let us say, to look upon those substances which in solution in water increase the normal hydrogen-ion concentration characteristic of pure water as acids and those which depress the hydrogen-ion concentration or in other words increase the hydroxyl-ion concentration, as bases. Leaving water aside for the moment and turning to liquid ammonia it may be said that all those compounds are acids which in solution in liquid ammonia bring about an increase in the hydrogen-ion concentration beyond that of the pure solvent. Now liquid ammonia, like water, is an excellent ionizing solvent while at the same time its autoionization is far below that of the latter solvent.<sup>4</sup>

It therefore follows on the basis of the above considerations that many compounds such as guanidine, the acid amides and amidines, may show acid properties in liquid ammonia, even though failing to do so in water solution.

**Hydrolysis of the Ammono Carbonic Acids.** When heated in the presence of water the ammono carbonic acids without exception, and including carbonic nitride, are hydrolyzed to aquo carbonic acid and ammonia, cyanamide for example as represented by the equation,  $\text{H}_2\text{NCN} + 2\text{H}_2\text{O} = \text{CO}_2 + 2\text{NH}_3$ . Inversely carbon dioxide has been ammonolyzed to guanidine and water,  $\text{CO}_2 + 3\text{NH}_3 = \text{H}_2\text{NC}(\text{NH})\text{NH}_2 + 2\text{H}_2\text{O}$ .<sup>5</sup>

#### AMMONO UNICARBONIC ACIDS

**Guanidine,  $\text{HN}=\text{C}(\text{NH}_2)_2$ .** *Preparation and Properties.* 1. The action of water and ammonia respectively on ethyl ortho carbonate might be expected to yield ortho carbonic acids as represented by the equations,



<sup>3</sup> The behavior of biguanide in liquid ammonia has not been investigated.

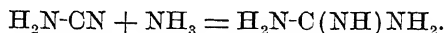
<sup>4</sup> Carvallo [*Ann. Phys.*, N. S., 2, 208, 224 (1914)]; cf. Franklin and Kraus, *J. Am. Chem. Soc.*, 27, 191 (1905)], prepared specimens of liquid ammonia showing a specific conductance as low as  $4.9 \times 10^{-11}$  Kohlrausch units. Comparing this value with that of pure water,  $4.0 \times 10^{-8}$ , it follows that the autoionization of liquid ammonia is of the order of a thousandth or less that of water.

<sup>5</sup> Blair, *J. Am. Chem. Soc.*, 48, 87 (1926).

As a matter of experimental fact, however, the products so obtained are carbon dioxide and ethyl alcohol in the one case, guanidine and ethyl alcohol in the other.<sup>6</sup> Guanidine thus appears as a deamination product of an hypothetical ortho ammono carbonic acid.

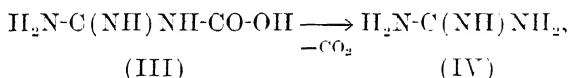
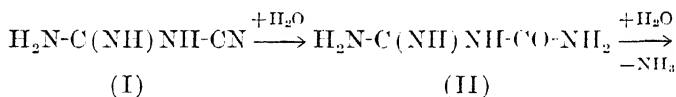
2. Good yields of guanidine have been obtained by heating carbon tetrachloride with highly compressed ammonia at 140°.<sup>7</sup> The equation  $\text{CCl}_4 + 3\text{NH}_3 = \text{HN}=\text{C}(\text{NH}_2)_2 + 4\text{HCl}$ , in accordance with which the reaction takes place, may be said to represent the ammonolysis of a carbonic acid chloride to an ammono carbonic acid.

3. Guanidine is formed by heating either cyanamide or dicyandiamide with ammonium salts.<sup>8</sup> The conversion of cyanamide into guanidine may be explained as consisting in the ammonation of the one ammono carbonic acid to the other,



According to Blair and Braham the formation of guanidine from dicyandiamide takes place in accordance with the scheme,  $\text{H}_2\text{N}-\text{C}(\text{NH})\text{NH}-\text{CN} \xrightarrow{+\text{NH}_3} \text{H}_2\text{N}-\text{C}(\text{NH})\text{NH}-\text{C}(\text{NH})\text{NH}_2 \xrightarrow{+\text{NH}_3} 2\text{H}_2\text{N}-\text{C}(\text{NH})-\text{NH}_2$ , which represents the ammonation of dicyandiamide first to biguanide and thence to guanidine.

4. By the action of moderately concentrated sulfuric acid at temperatures around 140° dicyandiamide is converted largely into guanidine.<sup>9</sup> Here according to Davis the reactions take the course,



which is to say that dicyandiamide (I) is first hydrated to dicyandiamidine (II), a mixed aquo-ammono carbonic acid, which is then hydrolyzed to the aquo-ammono carbonic acid (III) known as guanylecarbamic acid. This acid, being unstable in the free state, loses carbon dioxide thereby passing over into guanidine (IV).

5. Guanidine is formed when in liquid ammonia solution methyl-

<sup>6</sup> Hofmann, *Ann. Chem.*, **139**, 114 (1866); *Ber.*, **1**, 145 (1868).

<sup>7</sup> Stähler, *Ber.*, **47**, 909 (1914).

<sup>8</sup> Ewan and Young, *J. Soc. Chem. Ind.*, **40**, 109 (1921); Davis, *J. Am. Chem. Soc.*, **43**, 2234 (1921); Blair and Braham, *J. Am. Chem. Soc.*, **44**, 2342 (1922); *Ind. Eng. Chem.*, **16**, 848 (1924).

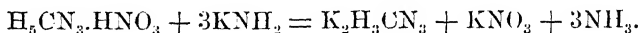
<sup>9</sup> Davis, *J. Am. Chem. Soc.*, **43**, 669 (1921).

amine is treated with iodine or when heated with ammonium azide. Furthermore guanidine is formed by the action of iodine on hydrocyanic acid in liquid ammonia solution. As will be explained later the conversion of methylamine into guanidine consists in the nitridation of an ammono alcohol into an ammono carbonic acid. (Cf. Chapter XXVIII, p. 229.) The conversion of hydrocyanic acid into guanidine involves the nitridation of an ammono carbonous acid or of formic acid anammonide to an ammono carbonic acid.

Guanidine has been obtained as a strongly alkaline, highly hygroscopic crystalline mass. In water solution it behaves as a strong monacid base which absorbs carbon dioxide with avidity and unites with mineral acids to form neutral salts.

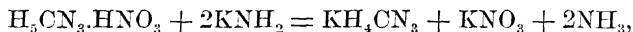
**Metallic Salts.** Regarding guanidine as an ammono carbonic acid it might be expected that in liquid ammonia solution it would act on metallic amides to form salts after the manner of the formation of salts by the interaction of acids and metallic hydroxides in water solution. As a matter of fact several metallic salts of guanidine have been so prepared. However guanidine nitrate instead of guanidine itself was used in the preparation of these salts for the reason that it appears to be very difficult, if not practically impossible, to prepare guanidine entirely free from water.<sup>10</sup>

*Dipotassium Guanidine*,  $\text{HN}\cdot\text{C}(\text{NHK})_2$ . Guanidine nitrate in liquid ammonia solution may be regarded as a mixture of aquo nitric acid and an ammono carbonic acid. When to such a solution potassium amide is added in excess potassium nitrate and the dipotassium salt of guanidine are formed,



Since potassium nitrate is easily soluble in liquid ammonia while dipotassium guanidine appears as an insoluble precipitate the separation of the two salts is easily accomplished. By the action of water dipotassium guanidine is vigorously hydrolyzed to guanidine and potassium hydroxide.

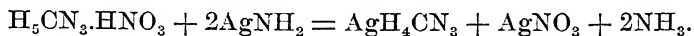
When guanidine nitrate and potassium amide were brought together in the proportion represented by the equation,



a solution was obtained which on concentration gave a crop of two distinct forms of crystals. Since the one form was recognized as crystals of potassium nitrate the other must have been crystals of monopotassium guanidine. However a monopotassium salt was not isolated and analyzed.

<sup>10</sup> Franklin, *J. Am. Chem. Soc.*, **44**, 490 (1922).

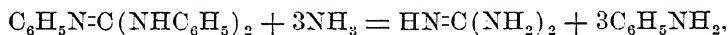
*Monosilver Guanidine*,  $\text{AgN}=\text{C}(\text{NH}_2)_2$ . When insoluble silver amide is digested for a time with a liquid ammonia solution of guanidine nitrate in excess monosilver guanidine and silver nitrate are formed,



With the silver amide completely converted into silver nitrate and silver guanidine, the latter salt becomes the only insoluble compound of the system and is consequently easily isolated.

Krall<sup>11</sup> obtained monosilver guanidine and disilver guanidine,  $\text{Ag}_2\text{H}_3\text{CN}_3$ , by adding silver nitrate to a strongly alkaline aqueous solution of guanidine nitrate. He obtained a copper salt,  $\text{CuH}_3\text{CN}_3$ , by treating a dilute water solution containing guanidine and a copper salt with alkali.

**Esters.** Looking upon guanidine as an ammono carbonic acid it follows that its numerous known alkyl and aryl derivatives are to be regarded as esters and as such to be ammonolyzable, N-N'-N''-triphenylguanidine for example to guanidine and aniline. Accordingly Niemann<sup>12</sup> found that in accordance with the equation,



guanidine and aniline are formed when N-N'-N''-triphenylguanidine and ammonium chloride are heated together in liquid ammonia for a time.

The failure of triphenylguanidine to undergo ammonolytic decomposition when heated with potassium amide in liquid ammonia solution may perhaps be interpreted as indicating that triphenylguanidine is an ester of such an extremely weak acid that in its ammonolytic behavior it resembles the ethers rather than the esters. However no definite line can be drawn between compounds called esters and those known as ethers. Every one agrees that dimethyl oxide is an ether and that methyl formate and dimethyl carbonate, for example, are esters. One avoids deciding whether the compound,  $\text{CH}_2(\text{OCH}_3)_2$ , is an ether or an ester by calling it an acetal.

**Ester Salts.** In view of the experimental difficulties in the way of preparing metallic salts of guanidine itself the attempt was made to accumulate evidence in support of the view that guanidine is an ammono carbonic acid by a study of the behavior of liquid ammonia solutions of triphenylguanidine toward a number of ammono bases. Triphenylguanidine is formally a triphenyl ester of an ammono carbonic acid and since it contains two hydrogen atoms attached

<sup>11</sup> Krall, *J. Chem. Soc.*, 107, 1396 (1915).

<sup>12</sup> Niemann, Thesis, Stanford University, 1926.



to nitrogen it is at the same time a dibasic acid which should react with metallic amides to form salts. Moreover in view of the fact that organic compounds in general are more or less soluble in liquid ammonia it was anticipated, and in fact found to be true, that the alkali metal salts of triphenylguanidine would be found sufficiently soluble to permit their purification by the ordinary processes of recrystallization.

Metallic salts of triphenylguanidine as follows have been prepared by the action of the acid-ester, in liquid ammonia solution, on the respective ammonio bases.<sup>13</sup>

*Dipotassium Triphenylguanidine*,  $C_6H_5N=C(NKC_6H_5)_2$

*Disodium Triphenylguanidine*,  $Na_2(C_6H_5)_3CN_3$  and  $Na_2(C_6H_5)_3CN_3 \cdot 3NH_3$

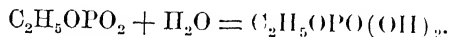
*Monosilver Triphenylguanidine*,  $AgH(C_6H_5)_3CN_3$  and  $AgH(C_6H_5)_3CN_3 \cdot NH_3$

*Cuprous Triphenylguanidine*,  $CuH(C_6H_5)_3CN_3$ .

*Monopotassium Diphenylguanidine*,  $KNC(NHC_6H_5)_2$ , has been prepared by the action of potassium amide on N-N'-diphenylguanidine in liquid ammonia solution.<sup>13a</sup>

**Metallic Salts of Dialkylguanidines.** The ester salts of guanidine described above were prepared by the action of N-N'-N''-triphenylguanidine on metallic amides which is to say that this acid ammonio ester acts on ammonio bases in a manner strictly analogous to the familiar action of aquo acids on aquo bases in water solution.

Griswold<sup>14</sup> has shown that potassium salts of N-N-dialkylguanidines are formed when N-N-dialkylcyanamides and potassium amide are brought together in liquid ammonia at temperatures around 0°. The reactions, which take place as represented by the equation,  $R_2NCN + KNH_2 = R_2NC(NH)NHK$ , consist in principle in the ammonation of esters of cyanamide to guanidine esters and are closely analogous to the reaction involved in the formation of guanidine from cyanamide by the addition of ammonia. These reactions are analogous furthermore to the known hydration of ethyl metaphosphate to ethyl orthophosphate,



Griswold prepared the potassium and sodium salts of N N dialkylguanidines named and formulated as follows.

*Potassium Dimethylguanidine*,  $(CH_3)_2N-C(NH)NHK$

*Potassium Diethylguanidine*,  $KH_2(C_2H_5)_2CN_3$

<sup>13</sup> Franklin, *J. Am. Chem. Soc.*, **44**, 490 (1922).

<sup>13a</sup> Griffith, Thesis, Stanford University, 1929.

<sup>14</sup> Gale Griswold, Thesis, Stanford University, 1926; Franklin, *J. Am. Chem. Soc.*, **55**, 4912 (1933).

*Potassium Di-n-propylguanidine*,  $\text{KH}_2(\text{C}_3\text{H}_7)_2\text{CN}_3$

*Potassium Di-isobutylguanidine*,  $\text{KH}_2(\text{C}_4\text{H}_9)_2\text{CN}_3$

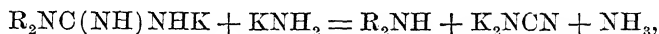
*Potassium Di-isoamylguanidine*,  $\text{KH}_2(\text{C}_5\text{H}_{11})_2\text{CN}_3$

*Sodium Diethylguanidine*,  $\text{NaH}_2(\text{C}_2\text{H}_5)_2\text{CN}_3$

*Sodium Di-isobutylguanidine*,  $\text{NaH}_2(\text{C}_4\text{H}_9)_2\text{CN}_3$ .

All these ester salts were obtained well crystallized and of sharply definite composition.

When gently warmed in solution with potassium amide these ester salts are decomposed to form metallic cyanamides and the respective dialkylamines as represented herewith,



instead of forming di- or tri-potassium salts of the dialkylguanidines perhaps might have been expected.

**Cyanamide**,  $\text{H}_2\text{NCN}$ ,  $\text{HN}=\text{C}=\text{NH}$ . All the known methods for the preparation of cyanamide and its salts as well as the many reactions in which cyanamide takes part are in complete harmony with the view that it is a carbonic acid.

*Formation.* Among the methods for the preparation of cyanamide either in the free state or in the form of its salts are the following.

1. The most familiarly known reaction for the formation of a salt of cyanamide is that concerned in the commercial preparation of calcium cyanamide. When calcium carbide is heated in the presence of nitrogen calcium cyanamide is formed in accordance with the equation,  $\text{CaC}_2 + \text{N}_2 = \text{CaCN}_2 + \text{C}$ , just as similar treatment with oxygen converts calcium carbide into carbonate of calcium,  $\text{CaC}_2 + 5\text{O} = \text{CaCO}_3 + \text{CO}_2$ . The two reactions are obviously closely analogous. The first equation represents the nitridation of calcium carbide to calcium ammonocarbonate, the latter its oxidation to calcium aquocarbonate. The carbon in excess of the amount required for the formation of respective carbonates appears in the one case in the free state, it is not nitridized to a carbonous or carbonic nitride, in the other it is oxidized to carbonic anhydride.

When calcium cyanamide is exposed to the action of superheated steam calcium aquocarbonate and ammonia are formed in accordance with the equation,  $\text{CaCN}_2 + 3\text{H}_2\text{O} = \text{CaCO}_3 + 2\text{NH}_3$ , which is to be read as representing the hydrolysis of a calcium ammonocarbonate to calcium aquocarbonate. Inversely when ammonia is passed over hot calcium carbonate<sup>15</sup> calcium cyanamide and water are formed. That is to say the above equation read from right to left represents the ammonolysis of calcium aquocarbonate to calcium ammonocarbonate.

In the abstract above referred to it is stated that barium and

<sup>15</sup> D. R. P., *Chem. Zentr.*, 1903, I, 677.

lead carbonates are converted into the respective salts of cyanamide in a similar manner. These observations have been confirmed in this laboratory and it has also been found that cyanamide salts of potassium, sodium and lithium are formed in small amounts when the carbonates of the respective metals are heated in an atmosphere of ammonia.

2. Sodium amide reacts with carbon at temperatures around  $350^{\circ}$  to  $400^{\circ}$  to form disodium cyanamide in a manner strictly analogous to the action of sodium hydroxide on highly heated carbon. The reactions involved are represented by the respective equations,  $2\text{NaNH}_2 + \text{C} = \text{Na}_2\text{CN}_2 + 4\text{H}$  and  $3\text{NaOH} + \text{C} = \text{Na}_2\text{CO}_3 + \text{Na} + 3\text{H}$ . In the first reaction carbon is nitridized to form a sodium ammonocarbonate, an equivalent amount of hydrogen being simultaneously reduced to elementary hydrogen. In the second reaction sodium aquocarbonate results from the oxidation of carbon while metallic sodium and hydrogen appear as reduction products.

3. The formation of sodium carbonate by the action of sodium hydroxide on carbon dioxide and of sodium cyanamide by the action of fused sodium amide on carbonic nitride,  $(\text{C}_3\text{N}_4)_x$ ,<sup>16</sup> as represented by the equations,  $2\text{NaOH} + \text{CO}_2 = \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$  and  $6\text{NaNH}_2 + \text{C}_3\text{N}_4 = 3\text{Na}_2\text{CN}_2 + 4\text{NH}_3$ , involves closely analogous reactions. In the one case the aquo base acting on the acid anhydride forms an aquocarbonate and water, in the other an ammonocarbonate and ammonia are formed by the action of the ammono base on carbonic anammonide. Not only carbonic nitride but the ammono carbonic acids in general are converted into sodium cyanamide by the action of an excess of fused sodium amide.<sup>17</sup>

4. All the ammono carbonic acids and aquo-ammonia carbonic acids as well as their many esters yield calcium cyanamide when heated with quicklime. Calcium cyanamide is the only calcium carbonate which is stable at high temperatures. Independently therefore of whatever intermediate reactions may take place Emich<sup>18</sup> uniformly observed the formation of calcium cyanamide when he heated his many carbonic acid derivatives with quicklime.

5. Cyanogen chloride is the nitrogen analog of carbonyl chloride. Such being the case it follows that just as water acts on carbonyl chloride to form aquo carbonic acid (carbon dioxide) so ammonia acts on cyanogen chloride, a carbonic nitride-chloride, to form cyanamide which thus again appears as an ammono carbonic acid. The parallel reactions are represented by the equations,  $\text{OCCl}_2 + 2\text{H}_2\text{O} = \text{OC}(\text{OH})_2 + 2\text{HCl}$  and  $\text{NCCl} + \text{NH}_3 = \text{NCNH}_2 + \text{HCl}$ .

<sup>16</sup> Unpublished observations.

<sup>17</sup> Franklin, *J. Am. Chem. Soc.*, **44**, 508 (1922).

<sup>18</sup> Emich, *Monatsh.*, **10**, 334 (1899).

*Properties.* In water solution cyanamide appears to be an entirely neutral substance. Such a solution neither shows an appreciable electrical conductance nor does it have any effect on ordinary indicators. In liquid ammonia solution on the other hand it certainly behaves as an acid in that it conducts electricity with fair facility,<sup>19</sup> sharply discharges the red color of a liquid ammonia solution of phenolphthalein made alkaline by the presence of potassium amide, attacks certain metals with the release of hydrogen, and reacts with alkali metal amides to form salts. Under the action of metallic zinc cyanamide in dilute hydrochloric acid solution is converted into methylamine<sup>20</sup> which is to say that an ammono carbonic acid undergoes reduction to an ammono methyl alcohol.

*Metallic Salts.* Making use of liquid ammonia as solvent in which to carry out the necessary reactions the following salts of cyanamide have been prepared.<sup>21</sup>

*Monopotassium Cyanamide*,  $\text{KHCN}_2\cdot\text{NH}_3$ . When cyanamide is added to an excess of potassium amide an amorphous, insoluble precipitate of the dipotassium salt is formed. This precipitate dissolves in a cyanamide solution to form a very soluble monopotassium salt which separates from cold concentrated solutions with one molecule of ammonia of crystallization.<sup>22</sup>

*Acid Magnesium Cyanamide*,  $\text{Mg}(\text{HCN}_2)_2\cdot 6\text{NH}_3$ ,  $\text{Mg}(\text{HCN}_2)_2\cdot 2\text{NH}_3$ . A liquid ammonia solution of cyanamide attacks metallic magnesium with a fairly vigorous evolution of hydrogen. After a time well-formed crystals of the composition represented by the first formula above separate from the solution. This ammonated salt, which is stable in vacuum at  $-33^\circ$ , loses ammonia when warmed in vacuum at  $20^\circ$  to form the diammonated salt. A product of the composition of the monammonated salt is obtained by heating the diammonated salt at  $100^\circ$  for a time.<sup>23</sup>

*Acid Calcium Cyanamide*,  $\text{Ca}(\text{HCN}_2)_2\cdot 2\text{NH}_3$ ,  $\text{Ca}(\text{HCN}_2)_2$ . Calcium amide, which is practically insoluble in liquid ammonia, is converted into a crystalline mass of the slightly soluble diammonated acid calcium cyanamide when allowed to stand in contact with a solution of cyanamide. Heated in vacuum at  $100^\circ$  the diammonated salt loses ammonia to form the anammonous salt.

Many metallic salts of cyanamide have long been known, among

<sup>19</sup> Franklin and Kraus, *J. Am. Chem. Soc.*, **27**, 195 (1905); Smith, *J. Am. Chem. Soc.*, **49**, 2164 (1927).

<sup>20</sup> Drechsel, *J. prakt. Chem.*, [2] **11**, 319 (1875).

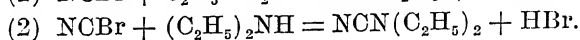
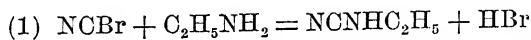
<sup>21</sup> Ruth V. Fulton, Thesis, Stanford University, 1925.

<sup>22</sup> Whether or not this compound may possibly be a salt of guanidine remains unknown.

<sup>23</sup> The statement of Franklin and Stafford [*Am. Chem. J.*, **27**, 103 (1902)] to the effect that they prepared a salt of the composition  $\text{MgNCN}$  must be erroneous.

them the acid calcium salt,  $\text{Ca}(\text{HCN}_2)_2$ , and the aquobasic calcium salt,  $(\text{HOCa})_2\text{CN}_2 \cdot 6\text{H}_2\text{O}$ .

**Esters. Formation.** 1. Looking upon cyanogen chloride as the nitrogen analog of carbonyl chloride then, just as the latter acid chloride acts on ethyl alcohol to form ethyl aquocarbonate, so the former should react with ethylamine and with diethylamine to form ethylcyanamide and diethylcyanamide respectively. The action of cyanogen chloride on primary and secondary amines has apparently never been investigated. However, cyanogen bromide is known to act on ethylamine and on diethylamine as represented by the equations,

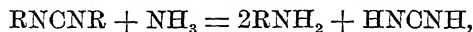
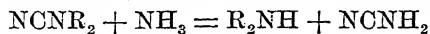
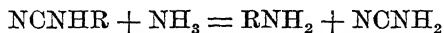


A carbonic acid bromide, so to say of the nitrogen system, acts on the respective ammono alcohols to form a monoethyl ammonocarbonate in the one case and an N-N-diethyl ammonocarbonate in the other.

2. Diethylcyanamide has also been prepared by the action of di-silver cyanamide on ethyl iodide. The close parallelism between this reaction and that involved in the formation of ethyl aquocarbonate by the action of silver aquocarbonate on ethyl iodide is obvious from a comparison of the equations,  $\text{NCNAg}_2 + 2\text{C}_2\text{H}_5\text{I} = \text{NCN}(\text{C}_2\text{H}_5)_2 + 2\text{AgI}$  and  $\text{OC}(\text{OAg})_2 + 2\text{C}_2\text{H}_5\text{I} = \text{OC}(\text{C}_2\text{H}_5)_2 + 2\text{AgI}$ , which represent the formation respectively of an ammono carbonic acid ester and an aquo carbonic acid ester.

3. A third method for the preparation of a dialkylcyanamide consists in the action of dimethylchloramine on potassium cyanide. The equation,  $(\text{CH}_3)_2\text{N} \cdot \text{Cl} + \text{KN} \equiv \text{C} = (\text{CH}_3)_2\text{N} \cdot \text{C} \equiv \text{N} + \text{KCl}$ , in accordance with which N-N-dimethylcyanamide and potassium chloride are formed does not represent a simple metathetic reaction. Intermolecular augmentation and reduction takes place whereby the carbonous acid carbon contained in potassium cyanide appears as carbonic acid carbon in the dimethylcyanamide while at the same time hypochlorous acid chlorine is reduced to hydrochloric acid chlorine.

**Ammonolysis.** If the alkyl and aryl derivatives of cyanamide are in fact ammono carbonic acid esters then, as the esters of aquo carbonic acid are readily hydrolyzed, so similar derivatives of cyanamide should undergo ammonolytic decomposition in accordance with the equations,



to form ammono alcohols and cyanamide.

Of the three classes of esters of the respective formulas given above it happens that representatives of the second class only have been investigated with respect to their ammonolytic behavior. Griswold<sup>24</sup> has shown that diethylcyanamide, dipropylcyanamide and diisobutylcyanamide are ammonolyzed quantitatively in accordance with the second of the above equations, when the respective esters are warmed to about 40° in liquid ammonia solution of potassium amide. Dipotassium cyanamide is formed on the one hand, diethylamine, dipropylamine and diisobutylamine respectively on the other.

It is interesting to note the striking contrast between the ammonolytic behavior of triphenylguanidine and the dialkyl derivatives of cyanamide. The former which is an ester of an extremely weak acid resists the action of potassium amide even at a temperature of 80° to 90°, whereas the esters of the latter relatively much stronger acid are ammonolyzed with the greatest ease.

**Ester-Salts.** A silver salt of phenylcyanamide,  $\text{Ag}(\text{C}_6\text{H}_5)\text{CN}_2$ , obtained by the action of silver nitrate on phenylcyanamide in solution either in aqua ammonia or in alcohol has long been known.<sup>25</sup> A potassium salt,  $\text{K}(\text{C}_6\text{H}_5)\text{CN}_2$ , of this acid ester is also known.<sup>26</sup>

#### AMMONO DICARBONIC ACIDS

**Biguanide,**  $\text{H}_2\text{N}-\text{C}(\text{NH})\text{NH}-\text{C}(\text{NH})\text{NH}_2$ . This is an ammono dicarbonic acid to which any one of a number of tautomeric formulas may be ascribed. It has been prepared by the deamination of guanidine,  $2\text{H}_2\text{N}^+\text{C}(\text{NH})\text{NH}_2 \longrightarrow \text{H}_2\text{N}-\text{C}(\text{NH})\text{NH}-\text{C}(\text{NH})\text{NH}_2$ , and by the ammonation of dicyandiamide,  $\text{H}_2\text{N}-\text{C}(\text{NH})\text{NH}-\text{CN} \xrightarrow{+\text{NH}_3} \text{H}_2\text{N}-\text{C}(\text{NH})\text{NH}-\text{C}(\text{NH})\text{NH}_2$ . The first reaction takes place when guanidine hydrochloride is heated alone, the second when dicyandiamide is heated in alcohol solution with ammonium chloride or when fused with ammonium nitrate.<sup>27</sup>

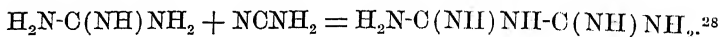
<sup>24</sup> Gale Griswold, Thesis, Stanford University, 1926; Franklin, *J. Am. Chem. Soc.*, **55**, 4912 (1933).

<sup>25</sup> Hofmann, *Ber.*, **18**, 3223 (1884).

<sup>26</sup> Hantzsch and Osswald, *Ber.*, **32**, 650 (1899).

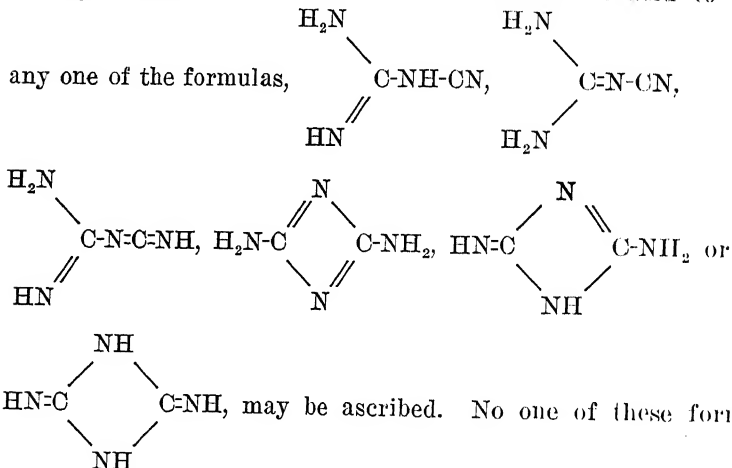
<sup>27</sup> Davis, *J. Am. Chem. Soc.*, **43**, 2234 (1921); Blair and Braham, *J. Am. Chem. Soc.*, **44**, 2342 (1922).

Biguanide is obtained in the form of its hydrated copper salt  $(C_2H_5N_5)_2Cu.2H_2O$ , when dicyandiamide is heated with an ammoniacal solution of cupric hydroxide. Finally biguanide is obtained in the form of its hydrochloride by the direct union of cyanamide and guanidine hydrochloride as represented by the equation,



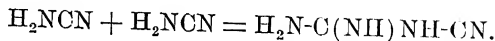
Examples of biguanide esters and ester-salts are phenylbiguanide,  $C_6H_5NH-C(NH)NH-C(NH)NH_2$ , its copper, nickel and cobalt salts,  $\alpha$ -diphenylbiguanide,  $(C_6H_5NH)_2C=N-C(NH)NH_2$ , and  $\beta$ -diphenylbiguanide,  $(C_6H_5)_2N-C(NH)NH-C(NH)NH_2$ . Attempts have not been made to prepare metallic salts of biguanide by means of reactions carried out in liquid ammonia solution.

**Dicyandiamide.** This is an ammono dicarbonic acid to which



has been established as representing the constitution of dicyandiamide.

When warmed in aqueous solution, with especial facility in the presence of ammonia, cyanamide is converted into dicyandiamide as represented by the equation,



The reaction involved in this dimerization of cyanamide to dicyandiamide is identical in principle with the ammonation of cyanamide to guanidine and with its hydration to urea. Inversely when dicyan-

<sup>28</sup> Joly, *Compt. rend.*, 102, 760 (1886).

diamide is heated with potassium amide in liquid ammonia solution it undergoes depolymerization to form cyanamide.<sup>29</sup>

When heated alone at a temperature somewhat above its melting point dicyandiamide is converted for the most part into melamine, which is a cyclic ammono tricarbonic acid, while at the same time a portion of the dicarbonic acid is depolymerized to cyanamide.<sup>30</sup> In water solution dicyandiamide behaves as a practically neutral substance.<sup>31</sup> In liquid ammonia solution it attacks potassium, magnesium and calcium and reacts with metallic amides after the manner of an acid.

**Metallic Salts.** Using liquid ammonia as solvent in which to carry out the reactions involved the following salts of this ammono dicarbonic acid have been prepared.<sup>32</sup>

*Monopotassium Dicyandiamide*,  $\text{H}_2\text{N}-\text{C}(\text{NH})\text{NK}-\text{CN}$

*Dipotassium Dicyandiamide*,  $\text{K}_2\text{H}_3\text{C}_2\text{N}_4$

*Magnesium Dicyandiamide*,  $\text{Mg}(\text{H}_3\text{C}_2\text{N}_4)_2 \cdot \text{NH}_3$

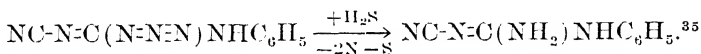
*Calcium Dicyandiamide*,  $\text{Ca}(\text{H}_3\text{C}_2\text{N}_4)_2 \cdot \text{NH}_3$ ,  $\text{Ca}(\text{H}_3\text{C}_2\text{N}_4)_2 \cdot 4\text{NH}_3$

*Cuprous Dicyandiamide*,  $\text{CuH}_3\text{C}_2\text{N}_4 \cdot 2\text{NH}_3$

*Monosilver Dicyandiamide*,  $\text{AgH}_3\text{C}_2\text{N}_4$ ,  $\text{AgH}_3\text{C}_2\text{N}_4 \cdot \text{NH}_3$ ,  $\text{AgH}_3\text{C}_2\text{N}_4 \cdot 2\text{NH}_3$

The diammonated silver salt has been obtained by the action of dicyandiamide, in liquid ammonia solution, on silver amide and on silver oxide. The ammonia free salt has been obtained by heating the ammonated salt and, as a crystalline precipitate, by adding ammonia to a water solution containing silver nitrate and dicyandiamide.<sup>33</sup>

*Phenyldicyandiamide*,  $\text{C}_6\text{H}_5\text{NH}-\text{C}(\text{NH})-\text{NH}-\text{CN}$ . This compound, first obtained by Wheeler and Jamieson,<sup>34</sup> and apparently the only ester of dicyandiamide on record, has been prepared by the reducing action of hydrogen sulfide on dicyanphenylamideazide as represented by the equation,



Nothing is known concerning the properties of this ester as an acid though the preparation by Hart of a sodium salt of dicyanphenylamideazide, which is stable in the presence of water, makes

<sup>29</sup> Hart, Thesis, Stanford University, 1926.

<sup>30</sup> Werner and Bell, *J. Chem. Soc.*, **117**, 1133 (1920).

<sup>31</sup> Bone and Perkin, *J. Chem. Soc.*, **67**, 416 (1895).

<sup>32</sup> Franklin, *J. Am. Chem. Soc.*, **44**, 501 (1922).

<sup>33</sup> Haag, *Ann. Chem.*, **122**, 22 (1862).

<sup>34</sup> Wheeler and Jamieson, *J. Am. Chem. Soc.*, **25**, 721 (1903).

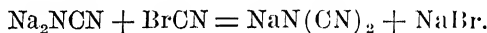
<sup>35</sup> Hart, *J. Am. Chem. Soc.*, **50**, 1924 (1928).



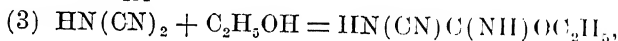
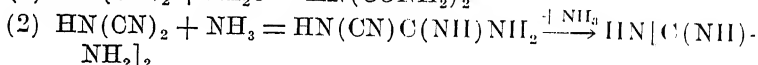
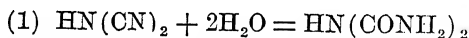
it highly probable that salts of this acid ester may be readily prepared.

**Dicyanimide,  $\text{HN}(\text{CN})_2$ .** When the copper salt of dicyanimide suspended in water, is decomposed by means of hydrogen sulfide a water solution of the free acid is obtained. Attempts to separate dicyanimide from solution have been unsuccessful because of the rapidity with which it polymerizes, and probably hydrolyzes, to insoluble, noncrystalline products of unknown composition.

The sodium salt has been obtained by the action of cyanogen bromide on disodium cyanamide in water solution.<sup>36</sup>



Dicyanimide is a strong monobasic acid water solutions of which dissolve sodium carbonate with the release of carbon dioxide, sharply redden litmus and are excellent conductors of electricity. It resembles cyanamide in its tendency to undergo polymerization and to react with water, ammonia and alcohol by direct addition. According to Madelung and Kern, under conditions which need not be considered here, dicyanimide unites with (1) water to form biuret, (2) with ammonia to form dicyandiamide and biguanide and (3) with ethyl alcohol to form O-ethylcyanurea. The equations in accordance with which these reactions take place,



represent, first, the hydration of the ammono dicarbonic acid to an aquo-ammono dicarbonic acid, second, its ammonation to the respective ammono dicarbonic acids indicated and third, its union with aquo ethyl alcohol to form an O-ethyl aquo-ammono-carbonate.

**Metallic Salts and Esters.** Using water as solvent the following salts have been prepared by Madelung and Kern and by Burdick.

*Sodium Dicyanimide,  $\text{NaN}(\text{CN})_2$*

*Ammonium Dicyanimide,  $\text{NH}_4\text{C}_2\text{N}_3$*

*Silver Dicyanimide,  $\text{AgC}_2\text{N}_3$*

*Cupric Dicyanimide,  $\text{Cu}(\text{C}_2\text{N}_3)_2$*

*Mercuric Dicyanimide,  $\text{Hg}(\text{C}_2\text{N}_3)_2$*

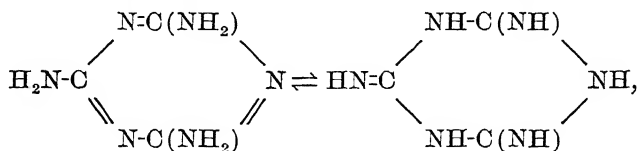
*Methyl Dicyanimide,  $\text{CH}_3\text{N}(\text{CN})_2$ .* This one known ester of dicyanimide was obtained by Madelung and Kern as a crystalline solid

<sup>36</sup> Madelung and Kern, *Ann. Chem.*, 427, 14 (1922); Burdick, *J. Am. Chem. Soc.*, 47, 1485 (1925).

by heating a benzene solution of methyl iodide in contact with silver dicyanamide in a closed tube at  $100^\circ$ ,  $\text{CH}_3\text{I} + \text{AgN}(\text{CN})_2 + \text{AgI}$ .<sup>37</sup>

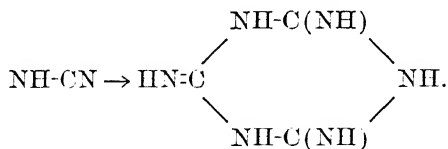
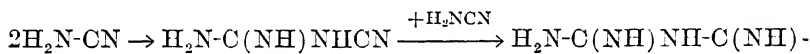
## AMMONO POLYCARBONIC ACIDS

**Melamine.** This cyclic ammono tricarbonic acid,



is obtained (1) when guanidine, guanidine carbonate, cyanamide or dicyandiamide is heated in the dry state, melam, melem and other products being formed at the same time, (2) along with ammeline and ammelide by heating salts of guanidine in aqua ammonia solution,<sup>38</sup> (3) in the form of beautiful crystals by heating liquid ammonia solutions of cyanamide or dicyandiamide at  $90^\circ$  for a time,<sup>39</sup> (4) by the action of ammonia on cyanuric chloride, on cyanuric acid esters and on trithiocyanuric acid esters.

The formation of melamine from cyanamide probably takes place as represented by the scheme,



By a process which is in principle ammonation two molecules of cyanamide unite to form dicyandiamide. A third molecule adds itself to the dicyandiamide molecule to form an unknown open chain ammono tricarbonic acid, which undergoing intramolecular ammonation, yields melamine.

In a similar manner, it may be assumed, two molecules of cyanamide react with one molecule of cyanic acid to form ammeline,  $2\text{H}_2\text{N}-\text{CN} + \text{HNCO} = \text{C}_3\text{H}_5\text{ON}_5$ , one molecule of cyanamide with two

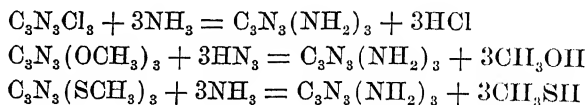
<sup>37</sup> Madelung and Kern, *Ann. Chem.*, **427**, 17 (1922).

<sup>38</sup> Krall, *J. Chem. Soc.*, **107**, 1399 (1915); Davis, *J. Am. Chem. Soc.*, **44**, 2595 (1922).

<sup>39</sup> Unpublished observations.

of cyanic acid to form ammelide,  $\text{H}_2\text{NCN} + 2\text{HNCN} = \text{C}_3\text{H}_4\text{O}_2\text{N}_3$ . The familiar trimerization of cyanic acid to cyanuric acid undoubtedly takes place in a similar stepwise fashion.

The formation of melamine by the action of ammonia on cyanuric chloride, on trimethylcyanurate and on trimethyltrithiocyanurate as represented by the equations,



involves the ammonolysis respectively of a cyclic carbonic acid nitride-chloride, an ester of a cyclic aquo-ammono tricarbonic acid and an ester of a cyclic thio-ammono tricarbonic acid. Melamine is also found among the products formed by heating ammonium thiocyanate,  $\text{NH}_4\text{SCN} \xrightarrow{-\text{H}_2\text{S}} \text{H}_2\text{NCN} \rightarrow \text{H}_6\text{C}_3\text{N}_6$ , and by heating melamine with ammonia,  $\text{H}_6\text{C}_3\text{N}_6 + \text{NH}_3 = 2\text{H}_6\text{C}_3\text{N}_6$ .<sup>40</sup>

Melamine is a base in the sense that it forms salts by direct union with acids. Contrary however to statements frequently made to the effect that it is a strong monacid base<sup>41</sup> it is, as a matter of fact a very weak base. In water solution it has no effect on litmus or on phenolphthalein. Moreover according to Liebig,<sup>42</sup> its hydrochloride in aqueous solution shows a strong acid reaction toward vegetable colors.

*Metallic Salts.* In liquid ammonia solution melamine attacks metallic potassium with the evolution of hydrogen and reacts with potassium amide after the manner of an acid. Two potassium salts and a silver salt have been prepared, *monopotassium melamine*,  $\text{KH}_6\text{C}_3\text{N}_6 \cdot \text{NH}_3$ , and *tripotassium melamine*,  $\text{K}_3\text{H}_3\text{C}_3\text{N}_6$ , by the action of potassium amide on melamine in liquid ammonia solution,<sup>43</sup> and *disilver melamine*,  $\text{Ag}_2\text{H}_4\text{C}_3\text{N}_6$ , by the action of aqua ammonia on the silver nitrate melamine addition product,  $2\text{AgNO}_3 \cdot \text{H}_6\text{C}_3\text{N}_6$ .<sup>44</sup>

*Esters.* Alkyl and aryl derivatives of melamine are known as endo and exo compounds depending upon whether the substituting groups are attached to cyclic or extra cyclic nitrogen as represented for the trimethyl esters, for example, by the formulas (II) and (V) (V') below.

The methods of preparation and the hydrolytic behavior of these compounds are in harmony with our assumption that they are car-

<sup>40</sup> Rathke, *Ber.*, 23, 1675 (1890).

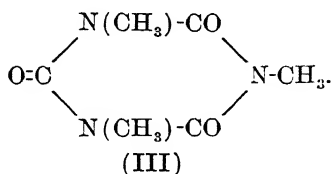
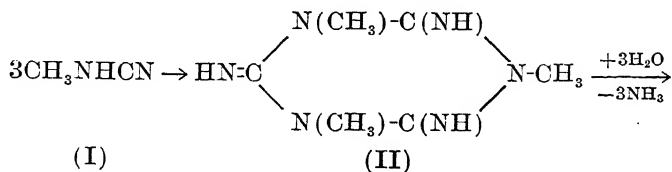
<sup>41</sup> Beilstein, *Handb. org. Chem.*, 3rd Ed., 1, 1444 (1893); Meyer and Jacobson, *Lehrb. org. Chem.*, 2nd Ed., 1, 2, 1337 (1913).

<sup>42</sup> Liebig, *Ann. Chem.*, 10, 19 (1834).

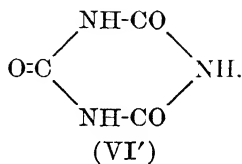
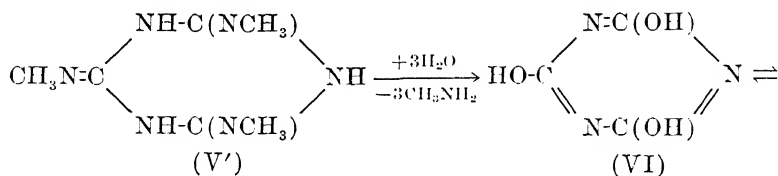
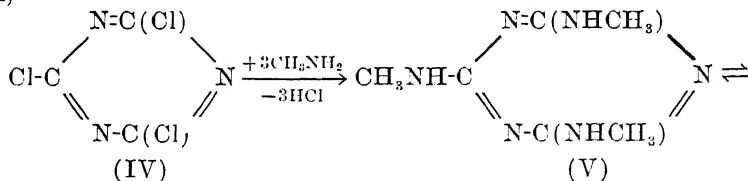
<sup>43</sup> Franklin, *J. Am. Chem. Soc.*, 44, 505 (1922).

<sup>44</sup> Zimmermann, *Ber.*, 7, 289 (1874). Not volume 9 as given in Beilstein, 3rd Ed.

bonic acid esters. The *exo* compound is formed by the polymerization of methylcyanamide and is hydrolyzed by the action of aqueous hydrochloric acid to trimethyl isocyanurate and ammonia,



The *exo* ester is formed by the action of methylamine on cyanuric acid chloride and is readily hydrolyzed to methylamine and cyanuric acid,

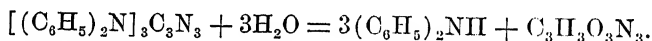


In accordance with the first scheme a methyl ester of an ammono unicarbonic acid trimerizes to a trimethyl ester of a cyclic ammono tricarbonic acid, (I) to (II), which in turn is hydrolyzed to an

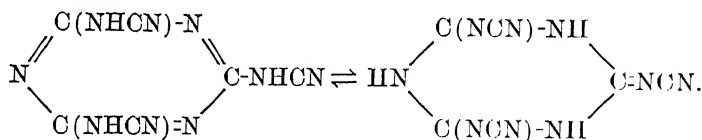
N-N'-N''-trimethyl ester of a cyclic aquo-ammono tricarmonic acid (III) and ammonia. In accordance with the second a cyclic tricarmonic acid nitride-chloride (IV) reacts with an ammono methyl alcohol to form a cyclic trimethyl ammonocarbonate (V)—an isomer of (II) and a tautomer of (V')—which hydrolyzes to an ammono alcohol and a cyclic aquo-ammono tricarmonic acid (VI) (VI').

Both the cyclic ester (III) and the cyclic acid (VI) (VI') when heated with water are hydrolyzed, the first to methylamine and carbon dioxide, the second to ammonia and carbon dioxide. The ammonolytic behavior of these compounds has not been investigated.

An example of an aryl ester of melamine is hexaphenylmelamine which has been made by the action of diphenylamine on cyanuric chloride,  $3(\text{C}_6\text{H}_5)_2\text{NH} + \text{C}_3\text{N}_3\text{Cl}_3 = [(\text{C}_6\text{H}_5)_2\text{N}]_3\text{C}_3\text{N}_3 + 3\text{HCl}$ . By the action of aqueous hydrochloric acid this ester is hydrolyzed to diphenylamine and cyanuric acid,



#### Tricyanmelamine,

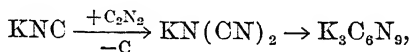


This cyclic hexacarbonic acid<sup>45</sup> is a trimer of dicyanamide just as melamine and cyanuric acid are trimers respectively of cyanamide and cyanic acid.

*Preparation and Properties.* Burdick obtained a specimen of the well-crystallized hydrated acid,  $\text{H}_3\text{C}_6\text{N}_9 \cdot 3\text{H}_2\text{O}$ , by evaporating an aqueous solution of the acid at low temperature, the solution having been made by the action of hydrogen sulfide on the silver salt suspended in water. At  $180^\circ$  the hydrated acid loses water of crystallization. When heated to a higher temperature the anhydrous acid polymerizes to melon. Tricyanmelamine shows conspicuously the properties of an acid in that its water solution sharply reddens litmus and is an excellent conductor of electricity. In water solution it is more or less rapidly converted into amorphous, insoluble products of unknown composition.

<sup>45</sup> Franklin, *J. Am. Chem. Soc.*, **44**, 497 (1922); Madelung and Kern, *Ann. Chem.*, **427**, 26 (1922); Burdick, *J. Am. Chem. Soc.*, **47**, 1485 (1925); Bannow, *Ber.*, **4**, 254 (1871), 13, 2201 (1880).

**Metallic Salts.** *Tripotassium Tricyanmelamine*,  $K_3C_6N_9$ .<sup>46</sup> When a mixture of potassium cyanide and mercuric cyanide is heated to dull redness a melt is obtained from which a limited amount of tripotassium tricyanmelamine can be extracted by means of hot water. The formation of the salt, it may be assumed, takes place in accordance with the scheme,

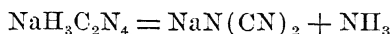


which represents first the nitridation of potassium ammonocarbonate to an ammonocarbonate, cyanogen from the mercuric cyanide functioning as nitridizing agent, and second the trimerization of dicyanimide to tricyanmelamine. The nature of the reduction product which is represented by C in the scheme remains unknown.

*Trisodium Tricyanmelamine*,  $Na_3C_6N_9$ ,  $Na_3C_6N_9 \cdot 3H_2O$ ,  $Na_3C_6N_9 \cdot 3NH_3$ , has been prepared by methods briefly described as follows.

1. By the action of fused sodium amide on a slight excess of melon Franklin obtained trisodium tricyanmelamine which he mistakenly called sodium dicyanimide. Burdick prepared the same salt by the action of fused sodium amide on an excess of dicyandiamide.

2. When the monosodium salt of dicyandiamide is heated it is converted into trisodium tricyanmelamine. It may be assumed that the acid salt first loses ammonia,



and that the sodium salt of dicyanimide thus formed undergoes polymerization to the trimeric form.

3. When sodium dicyanimide, prepared as described above by the action of cyanogen bromide on disodium cyanamide, is heated it is trimerized to trisodium tricyanmelamine.

Trisodium tricyanmelamine is moderately soluble in cold water and abundantly soluble in the hot solvent from which it separates in needle-like crystals containing three molecules of water of crystallization. It is also readily soluble in liquid ammonia from which solution it crystallizes with three molecules of ammonia. The hydrated salt loses its water of crystallization around  $160^\circ$ . The anhydrous salt melts at a higher temperature and then resists further change up to a temperature approaching redness when it decomposes into sodium cyanide, cyanogen and nitrogen. Boiled with aqueous sodium hydroxide it yields as final products sodium aquocarbonate and ammonia. Heated with water alone in a sealed tube it is converted into sodium carbonate, carbon dioxide and am-

<sup>46</sup> Franklin (ref. 45) mistakenly described this and other salts of tricyanmelamine as salts of dicyanimide.

monia. Water solutions of trisodium tricyanmelamine react alkaline with litmus.

*Monosodium Tricyanmelamine*,  $\text{NaH}_2\text{C}_6\text{N}_9$ ,  $\text{NaH}_2\text{C}_6\text{N}_9 \cdot 2\text{H}_2\text{O}$ . On acidifying a warm aqueous solution of trisodium tricyanmelamine and setting aside for a time the hydrated monosodium salt crystallizes from solution. This salt loses its water of crystallization on being heated.

Excepting as otherwise noted the following salts have been obtained from water solutions.

*Monammonium Tricyanmelamine*,  $\text{NH}_4\text{H}_2\text{C}_6\text{N}_9$ .

*Trisilver Tricyanmelamine*,  $\text{Ag}_3\text{C}_6\text{N}_9$ ,  $\text{Ag}_3\text{C}_6\text{N}_9 \cdot 3\text{NH}_3$ . The ammonated salt was prepared by the interaction of silver nitrate and trisodium tricyanmelamine in liquid ammonia solution.

*Magnesium Tricyanmelamine*,  $\text{Mg}_3(\text{C}_6\text{N}_9)_2$ ,  $\text{Mg}_3(\text{C}_6\text{N}_9)_2 \cdot 18\text{H}_2\text{O}$ .

*Barium Tricyanmelamine*,  $\text{Ba}_3(\text{C}_6\text{N}_9)_2$ ,  $\text{Ba}_3(\text{C}_6\text{N}_9)_2 \cdot 9\text{H}_2\text{O}$ .

*Cupric Tricyanmelamine*,  $\text{Cu}_3(\text{C}_6\text{N}_9)_2$ ,  $\text{Cu}_3(\text{C}_6\text{N}_9)_2 \cdot 9\text{H}_2\text{O}$ ,  $\text{Cu}_3(\text{C}_6\text{N}_9)_2 \cdot 12\text{NH}_3$ . On mixing cupric nitrate and trisodium tricyanmelamine in liquid ammonia solution the copper salt of tricyanmelamine separates in the form of blue crystals containing twelve molecules of ammonia.

*Acid Cupric Tricyanmelamine*,  $\text{Cu}(\text{H}_2\text{C}_6\text{N}_9)_2$ .

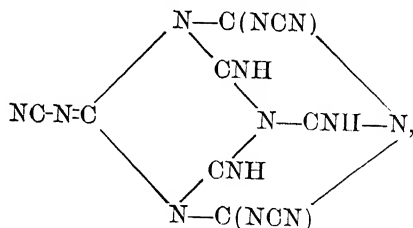
*Nickel Tricyanmelamine*,  $\text{Ni}_3(\text{C}_6\text{N}_9)_2 \cdot 9\text{H}_2\text{O}$ .

*Manganous Tricyanmelamine*,  $\text{Mn}_3(\text{C}_6\text{N}_9)_2$ .

*Lead Tricyanmelamine*,  $\text{Pb}_3(\text{C}_6\text{N}_9)_2 \cdot 6\text{NH}_3$ . When lead nitrate and trisodium tricyanmelamine are brought together in liquid ammonia solution a dense, white precipitate of the ammonated lead salt is formed.

*Tricyanmelamine Trimethylester*,  $(\text{CH}_3)_3\text{C}_6\text{N}_9$ . Madelung and Kern prepared this one known ester of tricyanmelamine by the interaction of methyl iodide and trisilver tricyanmelamine. Nothing is known of its ammonolytic behavior.

*Hydromelonic Acid*, *Cyamelon*,  $\text{H}_3\text{C}_9\text{N}_{13}$ .<sup>47</sup>

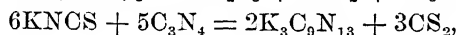
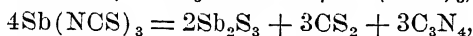
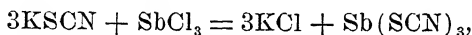


<sup>47</sup> According to Madelung and Kern,  $\text{NaH}_2\text{C}_6\text{N}_9 \cdot 3\text{H}_2\text{O}$ . The analytical data on the basis of which this formula was calculated are in somewhat better agreement with the formula,  $\text{NaH}_2\text{C}_6\text{N}_9 \cdot 2\text{H}_2\text{O}$ .

<sup>48</sup> Since the structure of hexamethylenetetramine as represented by the formula already given (p. 240) is to be taken as established it is reasonable to ascribe the above formula to hydromelonic acid.

This is a strong tribasic cyclic-ammono carbonic acid. It is known in the free state in water solution and in the form of metallic salts.<sup>49</sup>

**Metallic Salts.** *Tripotassium Melonate*,  $\text{K}_3\text{C}_9\text{N}_{13}$ ,  $\text{K}_3\text{C}_9\text{N}_{13}\cdot\text{H}_2\text{O}$ ,  $\text{K}_3\text{C}_9\text{N}_{13}\cdot 5\text{H}_2\text{O}$ . Liebig obtained the pentahydrate of this salt by heating a mixture of potassium thiocyanate and antimony chloride, extracting the resulting melt with water and evaporating the solution thus obtained to crystallization. Just what reactions are involved is not clear though in a general way it may be assumed that they follow the course represented by the equations,



which is to say that an unknown, and presumably unstable, antimony thio-ammono-carbonate (antimony thiocyanate) formed by the action of potassium thiocyanate on antimony chloride, breaks down to form antimony sulfide, carbon disulfide and carbonic nitride and that this carbonic anammonide reacts with potassium thio-ammono-carbonate to yield the potassium ammonocarbonate and carbon disulfide. Potassium melonate separates from water solution with five molecules of water of crystallization, four of which it loses at  $120^\circ$ . At  $150^\circ$  the anhydrous salt is formed.

*Dipotassium Melonate*,  $\text{K}_2\text{HC}_9\text{N}_{13}\cdot 3\text{H}_2\text{O}$ .

*Monopotassium Melonate*,  $\text{KH}_2\text{C}_9\text{N}_{13}$ . The water solution of this slightly soluble salt shows a strong acid reaction.

*Trisodium Melonate*,  $\text{Na}_3\text{C}_9\text{N}_{13}$ ,  $\text{Na}_3\text{C}_9\text{N}_{13}\cdot 5\text{H}_2\text{O}$ . Following Liebig's process for the preparation of potassium melonate and substituting sodium thiocyanate for the potassium salt Burdick obtained beautifully crystallized specimens of the pentahydrated sodium salt. At moderately elevated temperatures the hydrated salt loses its water of crystallization.

*Trisilver Melonate*,  $\text{Ag}_3\text{C}_9\text{N}_{13}$ ,  $\text{Ag}_3\text{C}_9\text{N}_{13}\cdot 6\text{NH}_3$ . On bringing sodium melonate and silver nitrate together in liquid ammonia solution a crop of colorless crystals of the hexammonated salt separates from the solution. The trisilver salt free from solvent of crystallization is obtained as a colorless, insoluble precipitate when silver nitrate is added to a water solution of tripotassium melonate.

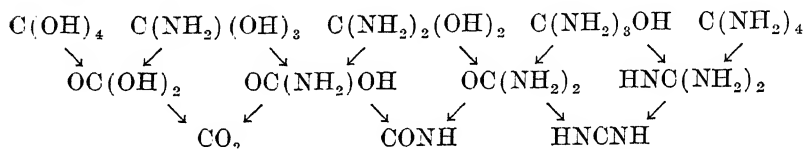
<sup>49</sup> Liebig, *Ann. Chem.*, **10**, 45 (1834); **50**, 337 (1844); **95**, 273 (1855); Volhard, *J. prakt. Chem.*, **9**, 29 (1836); Laurent and Gerhardt, *Ann. Chim.*, [3] **19**, 107 (1847); Burdick, *J. Am. Chem. Soc.*, **47**, 1484 (1925).



## CHAPTER XI.

### AQUO-AMMONO CARBONIC ACIDS.

Below are given the formulas for five hypothetical ortho carbonic acids together with the formulas for their dehydration and deamination products.



Of the ortho carbonic acids formulated the first is known in the form of esters only, the other four are quite unknown. Aquo carbonic acid, represented by the sixth formula, is known in the form of salts and esters but not in the free state. The ammono carbonic acids, the ninth and twelfth formulas, have been considered in the preceding chapter. A discussion of the three aquo-ammono carbonic acids represented by the seventh, eighth and eleventh formulas follows.

### AQUO-AMMONO UNICARBONIC ACIDS

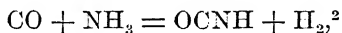
The three known aquo-ammono carbonic acids containing one carbon atom in the molecule are cyanic acid, carbamic acid and urea.

**Cyanic Acid**,  $\text{HNCN}$ ,  $\rightleftharpoons \text{HOCN}$ . If it could be assumed that the oxygen atom in cyanic acid is definitely bound by both its valences to the carbon atom as represented by the first of the above formulas then this compound, as a derivative of ammonia in which hydrogen is substituted by the acid-forming carbonyl group or as a derivative of water in which all the hydrogen is replaced by the CNH group, might properly be looked upon not as a mixed aquo-ammono carbonic acid but rather as a compound which is at the same time an ammono carbonic acid and carbonic anhydride. On the other hand the second formula may be said to represent an aquo carbonic acid carbonic anammonide. As a matter of fact cyanic acid, like all acid imides and amides, is a tautomeric compound and therefore without definite structure in so far as the attachment of the hydrogen atom is concerned. The acid is to be represented by either of the above formulas. The metallic salts of cyanic acid are aquo-

ammono-carbonates and as such may be represented by any one of the formulas,  $M-N\equiv C:O$ ,  $M-O-C\equiv N$  or  $(NCO)^- M^+$ , excepting that in the case of the mercuric salt, according to Hantzsch,<sup>1</sup> the metal is definitely attached to nitrogen.

In support of the view that cyanic acid is an aquo-ammono carbonic acid it will be worth while to pass in review some of the methods for making the acid and then to consider a few examples of its characteristic reactions.

*Formation.* 1. At high temperatures carbon monoxide, which may be said to be the anhydride of an hypothetical carbonous acid, is nitridized to cyanic acid by the action of ammonia,



just as under similar circumstances it is oxidized to carbon dioxide by the action of water. A mixed aquo-ammono carbonic acid is formed in the one case, an aquo carbonic acid or rather its anhydride in the other.

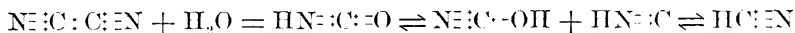
2. Cyanic acid, in the form of its potassium salt, is formed by the action of potassium hydroxide on cyanogen bromide. The reaction, which is represented by the equation,



consists, in principle, in the hydrolysis of a carbonic acid bromide to a potassium aquo-ammono-carbonate.

3. Potassium cyanate is formed by the action of oxidizing agents on potassium cyanide. Looking upon the latter compound as an ammonocarbonite of potassium, it follows that its conversion into potassium cyanate may be interpreted as consisting in the oxidation of potassium ammonocarbonite to a potassium aquo-ammono-carbonate.

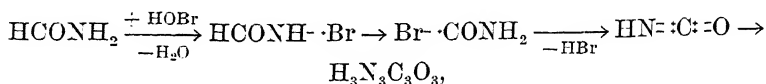
4. Potassium hydroxide acts on cyanogen to form potassium cyanate and potassium cyanide. Since the stage of augmentation of carbon in cyanogen when represented by the formula,  $N\equiv C-C\equiv N$ , lies between that of the carbon in hydrocyanic acid on the one hand and of the carbon in cyanic acid on the other, it may be said that the action of potassium hydroxide on cyanogen involves the augmentation of the one cyanogen group to cyanic acid and the reduction of the other to hydrocyanic acid as represented by the equation,



<sup>1</sup> Hantzsch, *Ber.*, 35, 2717 (1902).

<sup>2</sup> Jackson and Northall-Laurie, *J. Chem. Soc.*, 87, 433 (1905).

5. Cyanic acid, or rather its trimer cyanuric acid, is formed by the action of potassium hypobromite on formamide. Presumably a Hofmann rearrangement takes place,



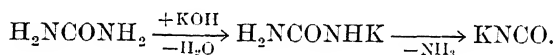
which involves the augmentation of formic acid carbon to carbonic acid carbon and the concomitant reduction of hypobromous acid bromine to hydrobromic acid bromine.

6. Potassium formamide, which is obtained by the action of potassium amide on formamide in liquid ammonia solution, readily decomposes to form potassium cyanate and hydrogen as represented by the equation,  $\text{HCONHK} = \text{KNC} \text{O} + \text{H}_2$ .<sup>3</sup> By intramolecular augmentation and reduction a formic acid salt is converted into a carbonate while hydrogen is at the same time reduced to the elementary state.

7. Cyanic acid in the form of its potassium salt is one of the products formed by the action of ammonia on hot potassium carbonate.<sup>4</sup> One may say that potassium aquocarbonate is thus ammonolyzed to a potassium aquo-ammono-carbonate. Potassium cyanamide, which is formed at the same time, is a product of the complete ammonolysis of potassium aquocarbonate.

8. When sodium carbamate is heated it loses water and passes over into sodium cyanate,  $\text{H}_2\text{NCOONa} = \text{NaNCO} + \text{H}_2\text{O}$ , the one aquo-ammono-carbonate undergoing dehydration to form the second.

9. Urea, when heated with alcoholic potassium hydroxide, is converted into potassium cyanate, assuming the intermediate formation of a potassium salt, in accordance with the equation,



Simply by heating urea in the dry state cyanic acid, along with other products, is formed.

*Reactions.* Cyanic acid and the cyanates enter into a very large number of reactions all of which may be regarded as involving the action of an aquo-ammono carbonic acid.

1. Cyanic acid reacts readily with water to form carbon dioxide and ammonia, which is to say that the aquo-ammono carbonic acid is hydrolyzed to aquo carbonic acid.

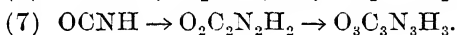
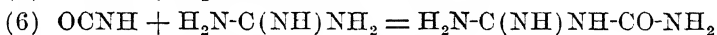
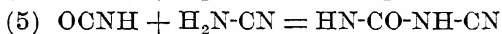
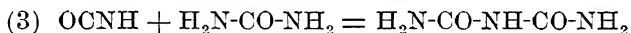
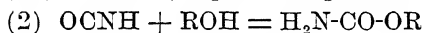
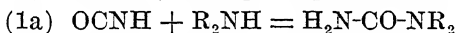
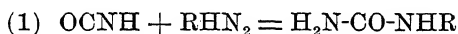
2. Wöhler's synthesis of urea by the rearrangement of ammonium

<sup>3</sup> Ruth V. Fulton, Thesis, Stanford University, 1925.

<sup>4</sup> Siepermann, *Ber.*, 20, Ref., 180 (1887).

cyanate may be explained as consisting simply in the ammonation of the monobasic aquo-ammono carbonic acid, to the formally tetrabasic aquo-ammono carbonic acid,  $\text{OCNH} + \text{NH}_3 = \text{OC}(\text{NH}_2)_2$ . Thus interpreted the reaction differs nowise in principle from the reactions involved in the hydration of any of the ordinary acid anhydrides and pyro acids.

3. Cyanic acid in the free state as well as in the form of its salts and esters enters into a large number of addition reactions which in principle are identical with the reaction involved in the formation of urea by the ammonation of cyanic acid and the hydration of an acid anhydride to an aquo acid. Thus cyanic acid unites, (1) (1a) with amines to form substituted ureas, (2) with alcohols to form carbamic acid esters, (3) with other aquo-ammono carbonic acids, with urea for example, to form biuret, (4) with carbamic acid esters to form esters of allophanic acid, (5) with ammono carbonic acids, such as cyanamide, to form cyanurea, and with guanidine (6) to form dicyandiamidine and finally even with itself (7) to form dicyanic acid and cyanuric acid. The respective reactions involved are represented by the equations,



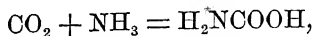
This conspicuous tendency on the part of cyanic acid to unite with alcohols, ammonia and the amines, with other carbonic acids and to undergo polymerization, properties which it shares with cyanamide and dicyanimide, is shown in a very subordinate degree, if at all, by aquo carbonic acid and carbon dioxide.

*Salts and Esters.* Many metallic salts and N-esters of cyanic acid are known of which potassium cyanate,  $\text{KOCN} \rightleftharpoons \text{KNCO}$ , and ethyl isocyanate,  $\text{C}_2\text{H}_5\text{NCO}$ , are examples. No O-esters of cyanic acid have been prepared.

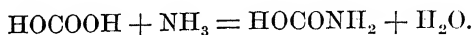
**Carbamic Acid,**  $\text{HO-CO-NH}_2 \rightleftharpoons \text{HO-C}(\text{NH})\text{OH}$ . This is a mixed aquo-ammono carbonic acid known in the form of salts, esters and ester-salts but not in the free state.

*Formation.* 1. Carbamic acid is obtained in the form of its ammonium salt when ammonia and carbon dioxide are brought to-

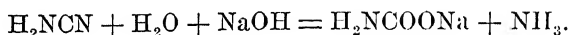
gether either in the gaseous state or in water solution. The reaction between the dry gases consists in the ammonation of carbonic anhydride to form an aquo-ammono carbonic acid,



which immediately unites with a second molecule of ammonia to form the ammonium salt. The same reaction, presumably, takes place in water solution, though it is possible in this case to interpret the reaction as consisting in the partial ammonolysis of an aquo carbonic acid to an aquo-ammono carbonic acid,



2. Just as carbamic acid is formed by the partial ammonolysis of aquo carbonic acid so also it is formed by the partial hydrolysis of an ammono carbonic acid. Cyanamide, for example, is hydrolyzed to sodium carbamate by the action of hot aqueous alcohol solution of sodium hydroxide,



*Reactions.* 1. Free carbamic acid decomposes into carbon dioxide and ammonia just as does aquo carbonic acid into carbon dioxide and water.

2. When ammonium carbamate is heated in a closed tube a considerable yield of urea results. One may say that the first aquo-ammono carbonic acid is thereby ammonolyzed to the second as represented by the equation,  $\text{H}_2\text{NCOOH} + \text{NH}_3 = \text{H}_2\text{NCONH}_2 + \text{H}_2\text{O}$ .

3. When hydrated sodium carbamate is strongly heated a residue of sodium carbonate is left behind. The sodium salt of an aquo-ammono carbonic acid is thereby hydrolyzed to sodium aquocarbonate and ammonia. Acid sodium carbonate is probably first formed,  $\text{H}_2\text{NCOONa} + \text{H}_2\text{O} = \text{HOCOONa} + \text{NH}_3$ , which at the higher temperature is converted into disodium carbonate.

*Metallic Salts.* Ammonium, sodium, potassium, calcium and strontium salts of carbamic acid have long been known. By the action of potassium amide on ammonium carbamate in liquid ammonia solution the monopotassium and dipotassium salts,  $\text{H}_2\text{NCOOK}$  and  $\text{KNHCOOK}$  or  $\text{HNC(OK)}_2$ , have been prepared.<sup>5</sup>

*Esters.* It will suffice present purposes to discuss but one of the many known esters of carbamic acid, namely urethane.

**O-Ethyl Carbamate, Urethane,  $\text{H}_2\text{N-CO-OC}_2\text{H}_5$ . Formation.**

<sup>5</sup> Blair, *J. Am. Chem. Soc.*, 48, 96 (1926).

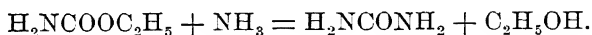
Five reactions whereby urethane has been prepared are given by the equations,

- (1)  $\text{H}_2\text{NCOC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OH} = \text{H}_2\text{NCOOC}_2\text{H}_5 + \text{HCl}$
- (2)  $\text{C}_2\text{H}_5\text{OCOC}_2\text{H}_5 + \text{NH}_3 = \text{C}_2\text{H}_5\text{OCONH}_2 + \text{HCl}$
- (3)  $\text{OC}(\text{OC}_2\text{H}_5)_2 + \text{NH}_3 = \text{H}_2\text{NCOOC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OH}$
- (4)  $\text{OCNH}_2 + \text{C}_2\text{H}_5\text{OH} = \text{H}_2\text{NCOOC}_2\text{H}_5$
- (5)  $\text{OC}(\text{NH}_2)_2 + \text{C}_2\text{H}_5\text{OH} = \text{H}_2\text{NCOOC}_2\text{H}_5 + \text{NH}_3$

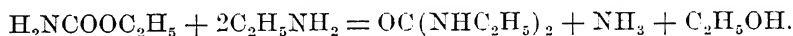
The first equation represents the formation of an ester by the action of an alcohol on an acid chloride, the second, by the ammonolytic action of ammonia on an ester-chloride. The third equation represents the partial ammonolysis of an aquo carbonic acid ester to an aquo-ammono carbonic acid ester. Equations (4) and (5) represent respectively the addition of ethyl alcohol (in principle hydration) to an aquo-ammono carbonic, and the partial esterification of an aquo-ammono carbonic acid.

*Reactions.* From among the many reactions which urethane has been observed to undergo the following have been selected for consideration here.

1. When heated with aqueous ammonia urethane, which is an O-ester of an aquo-ammono carbonic acid, is ammonolyzed to urea and aquo ethyl alcohol,



2. When treated with ethylamine urethane is converted into symmetrical diethylurea in accordance with the equation,



The action of ethylamine on the acid amide group present in urethane is analogous to the action of ordinary alcohol on an aquo acid to form an aquo ester. The replacement of the ethoxy group by the ethylamine group constitutes, in principle, an ammonolytic reaction.

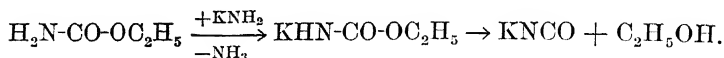
*Ester-Salts.* The acid properties of urethane are shown by the existence of a sodium salt,  $\text{NaNHCOOC}_2\text{H}_5$ , a silver salt,  $\text{AgNH}(\text{COOC}_2\text{H}_5)$ , a mercuric salt,  $\text{HgNCOOC}_2\text{H}_5$ ,<sup>6</sup> and by its slight, though distinct, electrical conductivity of its solutions in liquid ammonia.<sup>7</sup>

Attempts made to prepare a potassium salt of urethane by the action of potassium amide on urethane in liquid ammonia solution

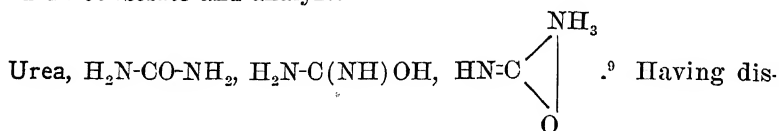
<sup>6</sup> Ley and Shafer, *Ber.*, 35, 1316 (1902). The silver salt is not registered in Beilstein.

<sup>7</sup> Franklin and Kraus, *J. Am. Chem. Soc.*, 27, 196 (1905).

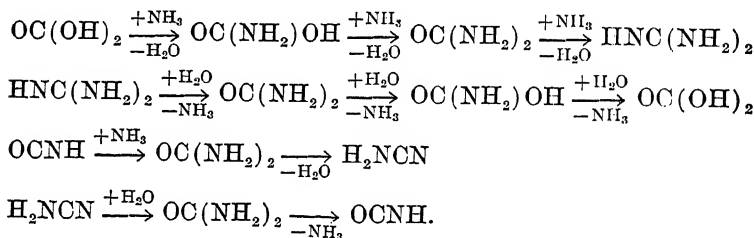
resulted in the formation of potassium cyanate and ethyl alcohol, presumably by way of a potassium salt of urethane as represented by the scheme,



Blair observed the formation of a well-crystallized intermediate product, presumably the potassium salt of urethane, which however he did not isolate and analyze.<sup>8</sup>



cussed cyanic acid and carbamic acid in some detail it will suffice present purposes to summarize the relations of urea to these aquo-ammonio carbonic acids and to the ammonio carbonic acids cyanamide and guanidine by means of the schemes,



The first scheme represents the ammonolysis of aquo carbonic acid successively to carbamic acid, urea and guanidine, the second, the stepwise hydrolysis of the ammonio carbonic acid to aquo carbonic acid. Excepting that the formation of carbamic acid may consist in the direct ammonation of carbon dioxide and that the inverse conversion of carbamic acid into carbon dioxide and ammonia may involve direct dissociation, all the reactions represented by these two schemes have been established experimentally. The third scheme represents the ammonation of cyanic acid to urea and the dehydration of urea to cyanamide while inversely the fourth represents the hydration of cyanamide to urea and the deammonation of urea to cyanic acid. These reactions are also known.

**Metallic Salts.** In water solution urea appears to be a strictly neutral if not a slightly alkaline substance. When dissolved in

<sup>8</sup> Blair, *J. Am. Chem. Soc.*, 48, 99 (1926).

<sup>9</sup> E. A. Werner [*J. Chem. Soc.*, 103, 694 (1918)] stoutly defends this formula as representing the constitution of urea.

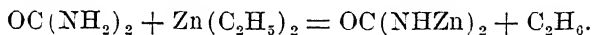
liquid ammonia it distinctly lowers the high electrical resistance of this solvent, it reacts with the alkali metals and magnesium with the evolution of hydrogen and with potassium amide to form a monopotassium and a dipotassium salt.<sup>10</sup>

*Monopotassium Urea*,  $\text{H}_2\text{N}\cdot\text{CO}\cdot\text{NHK}$ , has been obtained well crystallized by the action of potassium amide on an excess of urea in liquid ammonia solution. The salt dissolves readily in excess of urea but is practically insoluble in the pure solvent.

*Dipotassium Urea*,  $\text{OC}(\text{NHK})_2$ . When urea is added to an excess of potassium amide in liquid ammonia solution an insoluble, amorphous precipitate of the dipotassium salt is formed.

*Disilver Urea*,  $\text{OC}(\text{NHAg})_2$ . By the action of a water solution of urea on silver oxide a disilver salt is formed.<sup>11</sup>

*Zinc Urea*. Gal<sup>12</sup> reports the formation of a zinc salt of urea by the action of zinc ethyl on urea in ether solution,



Although there can be but little doubt concerning the nature of Gal's product its composition was apparently not confirmed by analysis.

*Mercury Urea Compounds*. In the fourth edition of Beilstein<sup>13</sup> the compounds formed by the action of urea on mercuric oxide and on mercuric salts are formulated as derivatives of the divalent radical,  $\text{OC}(\text{NHHg})_2$ , to which the name mercurio urea<sup>14</sup> has been given. Accordingly the compounds represented by the formulas,  $\text{OC}(\text{NH}\cdot\text{Hg}\cdot\text{OH})_2$  and  $\text{OC}(\text{NH}\cdot\text{Hg}\cdot\text{NO}_2)_2$ , to take two examples, are assumed to be respectively an hydroxide and a nitrate of dimercuro urea. Much more reasonably, it would seem, the first compound may be looked upon as an aquobasic mercuric salt of urea, that is to say as an aquobasic aquo-ammono-carbonate, the second as a mixed aquonitrate aquo-ammono-carbonate of mercury.<sup>15</sup>

**Esters.** Examples of reactions involved in the preparation of

<sup>10</sup> Blair, *J. Am. Chem. Soc.*, **48**, 97 (1926); Franklin and Stafford, *Am. Chem. J.*, **28**, 97 (1902).

<sup>11</sup> It is an interesting fact that silver and mercury especially, and a few other metals less conspicuously, are capable of forming salts with extremely weak ammonio and aquo-ammono acids which withstand the hydrolytic action of water and aqua ammonia and in some cases even of potassium hydroxide. Without thereby in any wise assuming that anything is being explained the workers in this laboratory have acquired the habit of referring to such metals as azophiles.

<sup>12</sup> Gal, *Bull. soc. chim.*, [2] **39**, 647 (1883).

<sup>13</sup> *Handb. org. Chem.*, **3**, 56 (1921).

<sup>14</sup> Ruspagliari, *Gazz. chim. ital.*, **27**, *I*, 1 (1897).

<sup>15</sup> The formula,  $\text{OC}(\text{NHHgOH})_2$ , represents a compound which is formally at the same time an acid salt and a basic salt. However, the acid properties of the third and fourth hydrogen atoms of the urea molecule may be assumed to be practically nonexistent. If this be done then the designation of this mercury compound as a basic salt becomes justified.

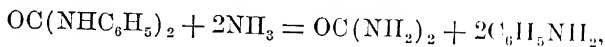


alkyl and aryl esters of urea are represented by the following equations.

- (1)  $\text{OCNC}_2\text{H}_5 + \text{NH}_3 = \text{H}_2\text{NCONHC}_2\text{H}_5$
- (2)  $\text{C}_6\text{H}_5\text{NHCOOC}_2\text{H}_5 + \text{NH}_3 = \text{C}_6\text{H}_5\text{NHCONH}_2 + \text{C}_2\text{H}_5\text{OH}$
- (3)  $\text{C}_6\text{H}_5\text{NHCN} + \text{H}_2\text{O} = \text{C}_6\text{H}_5\text{NHCONH}_2$
- (4)  $\text{OC}(\text{NH}_2)_2 + 2\text{C}_6\text{H}_5\text{NH}_2 = \text{OC}(\text{NHC}_6\text{H}_5)_2 + 2\text{NH}_3$
- (5)  $\text{OCNH} + (\text{C}_2\text{H}_5)_2\text{NH} = (\text{C}_2\text{H}_5)_2\text{NCONH}_2$
- (6)  $(\text{CH}_3)_2\text{NCN} + \text{H}_2\text{O} = (\text{CH}_3)_2\text{NCONH}_2$
- (7)  $(\text{C}_6\text{H}_5)_2\text{NCOCl} + \text{C}_6\text{H}_5\text{NH}_2 = (\text{C}_6\text{H}_5)_2\text{NCONHC}_6\text{H}_5 + \text{HCl}$
- (8)  $\text{OCCl}_2 + 2(\text{C}_2\text{H}_5)_2\text{NH} = (\text{C}_2\text{H}_5)_2\text{NCON}(\text{C}_2\text{H}_5)_2 + 2\text{HCl}$
- (9)  $\text{H}_2\text{NCN} + \text{CH}_3\text{OH} = \text{CH}_3\text{OC}(\text{NH})\text{NH}_2$
- (10)  $(\text{C}_6\text{H}_5)_2\text{NCN} + \text{C}_2\text{H}_5\text{OH} = \text{C}_2\text{H}_5\text{CO}(\text{NH})\text{N}(\text{C}_6\text{H}_5)_2$

Equation 1 represents the ammonation of ethyl isocyanate to N-ethylurea; equation 2, the ammonolysis of N-phenyl-O-ethyl carbamate to N-phenylurea; equation 3, the hydration of phenylcyanamide to N-phenylurea; equation 4, the action of aniline on urea to form N-N-diphenylurea; equation 5, the formation of N-N-diethylurea by the interaction of potassium cyanate and diethylammonium sulfate, in principle the ammonation of cyanic acid to an ester of urea; equation 6, the hydration of N-N-dimethylcyanamide to N-N-dimethylurea; equation 7, the action of aniline on a carbonic acid ester-chloride to form N-N-N'-triphenylurea; equation 8, the action of carbonic oxide-chloride on an ammono ethyl alcohol to form N-N-N'-N'-tetraethylurea; equation 9, the formation of O-methylurea by the interaction of cyanamide and sodium methylate; equation 10, the addition of aquo ethyl alcohol to a diethyl ammonocarbonate to form O-ethyl-N-N-diethylurea. All these derivatives of urea are to be regarded as esters of an aquo-ammono carbonic acid.

*Ammonolysis of Urea Esters.* Two urea esters, namely N-N'-diphenylurea and N-methylurea, have been investigated in respect to their ammonolytic behavior in liquid ammonia solution. When the first compound is heated in this solvent in the presence of ammonium chloride it is ammonolyzed to aniline, urea and guanidine.<sup>16</sup> It is probable that urea and aniline are first formed,

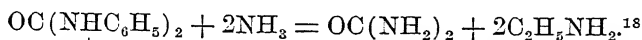


and that then a portion of the urea is ammonolyzed to guanidine<sup>17</sup>

<sup>16</sup> Niemann, Thesis, Stanford University, 1926.

<sup>17</sup> Blair [*J. Am. Chem. Soc.*, **48**, 87 (1926)] has shown that urea heated in liquid ammonia solution with ammonium chloride is ammonolyzed to guanidine,  $\text{OC}(\text{NH}_2)_2 + \text{NH}_3 = \text{HNC}(\text{NH}_2)_2 + \text{H}_2\text{O}$ , equilibrium becoming established when about 25 per cent of the urea is converted into guanidine.

though of course it is possible that a part of the diphenylurea is first ammonolyzed to diphenylguanidine and thence to guanidine and aniline. At 150° N-N'-diphenylurea is ammonolyzed by the action of alcoholic ammonia to urea and aniline,

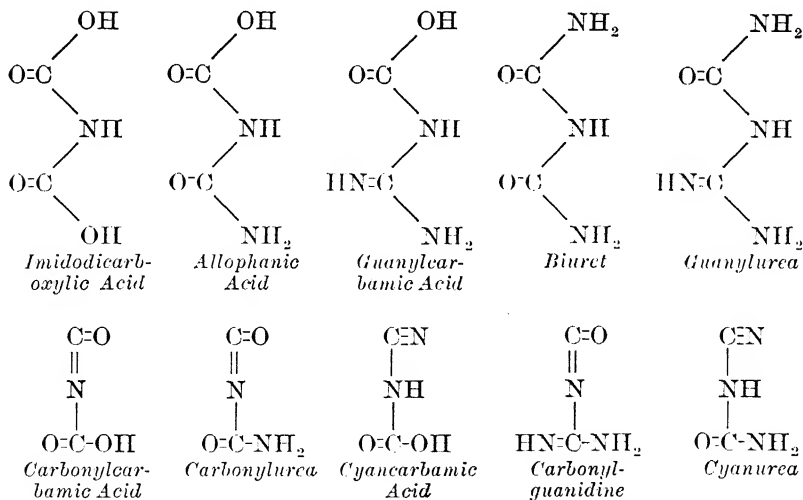


Blair identified methylamine, urea and guanidine as products of the ammonolytic decomposition of methylurea.

**Ester-Salts.** Alkyl and aryl derivatives of urea in which one or more of the urea hydrogen atoms remain unreplaced are formally acid esters and as such should be capable of forming metallic salts. Accordingly a mercuric salt of ethylurea  $(\text{C}_2\text{H}_5\text{NHCONH})_2\text{Hg}$ ,<sup>19</sup> a silver salt of O-methyl-N-phenylurea,<sup>20</sup>  $\text{C}_6\text{H}_5\text{NHC}(\text{OCH}_3)\text{NAg}$ , a sodium salt,<sup>21</sup>  $\text{C}_6\text{H}_5\text{NHCONHNa}$ , and a potassium salt,<sup>22</sup>  $\text{C}_6\text{H}_5\text{-NHCONHK}$ , of phenylurea have been prepared, the last salt well crystallized by the action of potassium amide on phenylurea in liquid ammonia solution.

#### AQUO-AMMONO DICARBONIC ACIDS

The following formulated and named aquo-ammono dicarbonic acids are theoretically possible all of which with the exception of carbonylurea and carbonylguanidine are known in the free state or in the form of esters.



<sup>18</sup> Claus, *Ber.*, **9**, 693 (1876).

<sup>19</sup> Leuckhardt, *J. prakt.*, [2] **21**, 18 (1880).

<sup>20</sup> Bruce, *J. Am. Chem. Soc.*, **26**, 434 (1904).

<sup>21</sup> Blacher, *Ber.*, **28**, 432 (1895).

<sup>22</sup> Unpublished observation.

Since polycarbonic acids in which carbon atoms are held together by means of oxygen, as represented for example by the formula,  $\text{HO-CO-O-CO-OH}$ , for an unknown pyrocarbonic acid, are apparently incapable of existence,<sup>23</sup> such unions have been ignored in developing the above scheme. Furthermore, it is to be observed that dicarbonic acids more highly hydrated or ammonated than those formulated in the upper horizontal row above have never been prepared.

Something of the extent to which salts, esters and ester-salts of these aquo-ammonio dicarbonic acids are known is given in the following pages. References, in general, are omitted except in connection with those compounds which are not registered in the fourth edition of Beilstein. Furthermore, in general each acid will be represented by but one of its possible tautomeric formulas.

1. **Imidodicarboxylic Acid, Carboxycarbamic Acid,  $\text{HO-CO-NH-CO-OH}$** , is known in the form of esters and ester-salts but not in the free state or in the form of salts. The potassium,  $\text{KN}(\text{COOC}_2\text{H}_5)_2$ , sodium,  $\text{C}_2\text{O}_4\text{N}(\text{C}_2\text{H}_5)_2\text{Na}$ , and silver,  $\text{C}_2\text{O}_4\text{N}(\text{C}_2\text{H}_5)_2\text{Ag}$ , salts of the diethyl ester have been prepared.

2. **Allophanic Acid, Carboxyurea,  $\text{H}_2\text{N-CO-NH-CO-OH}$** . Liebig and Wöhler<sup>24</sup> had the sodium, potassium, calcium and barium salts of allophanic acid, unknown in the free state, in their hands but established by analysis the composition of the barium salt,  $(\text{H}_2\text{N-CO-NH-CO-O})_2\text{Ba}$ , only. A disodium salt of allophanic acid,  $\text{C}_2\text{H}_2\text{O}_3\text{N}_2\text{Na}_2$ , has also been prepared.<sup>25</sup>

The acid properties of ethyl allophanate,  $\text{H}_2\text{N-CO-NH-CO-OC}_2\text{H}_5$ , are shown by the existence of a disilver salt,  $\text{C}_2\text{H}_2\text{O}_3\text{N}_2(\text{C}_2\text{H}_5)\text{Ag}_2$ ,<sup>26</sup> and a monopotassium salt,  $\text{C}_2\text{H}_2\text{O}_3\text{N}_2(\text{C}_2\text{H}_5)\text{K}$ ,<sup>27</sup> the latter having been obtained by the action of potassium amide on ethyl allophanate in liquid ammonia solution.

Trithioallophanic acid,  $\text{H}_2\text{N-CS-NH-CS-SH}$ , has been prepared as have also its potassium, and copper salts,  $\text{C}_2\text{H}_3\text{N}_2\text{S}_3\text{K}$  and  $(\text{C}_2\text{H}_3\text{N}_2\text{S}_3)_2\text{Cu}$ .

3. **Guanylcarbamic Acid, Carboxyguanidine,  $\text{H}_2\text{N-C}(\text{NH})\text{NH-CO-OH}$** , is known only in the form of its O-ethyl ester. No metallic salts either of the acid or of the acid ester have been prepared.<sup>28</sup>

4. **Biuret,  $\text{H}_2\text{N-CO-NH-CO-NH}_2$** . That biuret possesses acid prop-

<sup>23</sup> It is noted however that an ester of a mixed aquo-thio-ammonio dicarbonic acid is on record to which the formula,  $\text{C}_6\text{H}_5(\text{C}_2\text{H}_5)\text{NCS-O-CSN}(\text{C}_2\text{H}_5)\text{C}_6\text{H}_5$ , has been ascribed [Billeter, *Ber.*, 20, 1629 (1887)].

<sup>24</sup> Liebig and Wöhler, *Ann. Chem.*, 59, 295 (1846).

<sup>25</sup> Ephraim, *Ber.*, 35, 779 (1902).

<sup>26</sup> Dains, Greider and Kidwell, *J. Am. Chem. Soc.*, 41, 1005 (1919).

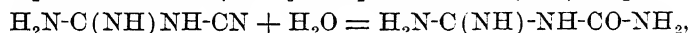
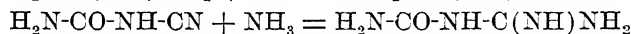
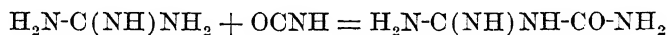
<sup>27</sup> Blair, *J. Am. Chem. Soc.*, 48, 102 (1926).

<sup>28</sup> Pinck and Blair, *J. Am. Chem. Soc.*, 49, 509 (1927).

erties is shown by its reacting in excess with potassium amide in liquid ammonia solution to form a monopotassium salt,  $C_2H_4O_2N_3K$ , with the ammonio base in excess to form a tripotassium salt,  $C_2H_2O_2N_3K_3$ ,<sup>29</sup> and further by the existence of a disilver salt,  $C_2H_3O_2N_3Ag_2$ , and two basic mercuric salts which may be represented by the respective formulas,  $Hg(NH-CO-NH-CO-NH-HgOH)_2$  and  $H_2N-CO-NH-CO-NH-HgOH$ .

N-alkyl and N-aryl esters of biuret are known in considerable number while at least one O-ester, namely, O-ethylbiuret,  $H_2N-CO-NH-C(NH)OC_2H_5$ , has been prepared.<sup>30</sup> None of these esters is known to form metallic salts.

5. Dicyandiamidine, Guanylurea,  $H_2N-C(NH)NH-CO-NH_2$ . Three of the simpler procedures for the preparation of this dicarbonic acid are summarized by means of the equations,



which represent the results obtained, first, by heating guanidine hydrochloride with potassium cyanate, second, by heating the silver salt of cyanurea with a water solution of ammonium chloride, and third, by the action of dilute mineral acids on dicyandiamide. The first equation represents the union of two unicarbonic acids to form a dicarbonic acid strictly after the manner of the ammonation of cyanic acid to urea, the second, the ammonation of cyanurea after the manner of the conversion of cyanamide to guanidine and of cyanic acid to urea. The third equation represents the hydration of dicyandiamide, which is an ammono dicarbonic acid, to an aquo-ammono dicarbonic acid.

Copper, nickel and palladium salts of dicyandiamidine of the respective formulas,  $(C_2H_5ON_4)_2Cu \cdot 2H_2O$ ,  $(C_2H_5ON_4)_2Ni \cdot 2H_2O$  and  $(C_2H_5ON_4)_2Pd \cdot 2H_2O$ , have been made.

6. Carbonylcarbamic Acid, Carboxyisocyanate,  $OC=N-CO-OH$ , is known in the form of its ethyl ester,  $OC=N-CO-OC_2H_5$ .

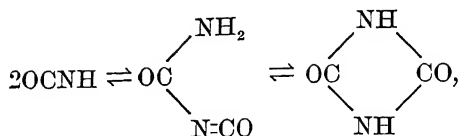
7. Carbonylurea, Carbamylisocyanate, Dicyanic Acid,  $H_2N-CO-N=CO$ . Davis and Blanchard<sup>31</sup> have shown that dicyanic acid, which has not been isolated, is present in water solutions of cyanic acid. The scheme,<sup>32</sup>

<sup>29</sup> Blair, *J. Am. Chem. Soc.*, **48**, 100 (1925).

<sup>30</sup> Madelung and Kern, *Ann. Chem.*, **427**, 24 (1922).

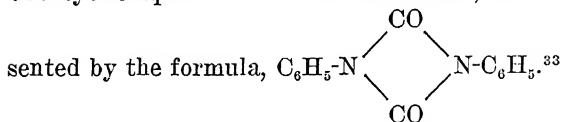
<sup>31</sup> Davis and Blanchard, *J. Am. Chem. Soc.*, **51**, 1806 (1929).

<sup>32</sup> Omitting other obvious tautomeric formulas.



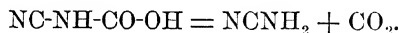
in accordance with which dicyanic acid is formed by the dimerization of cyanic acid, represents the dimer as existing in solution as an open chain and a cyclic aquo-ammonio dicarbonic acid in tautomeric equilibrium.

Apparently the only known esters of dicyanic acid are derivatives of the cyclic form. For example, it has been shown that diphenyl-diisocyanate, which is to be looked upon as an N-N'-diphenyl ester of a cyclic aquo-ammonio dicarbonic acid, has the constitution represented by the formula,



**8. Cyancarbamic Acid, Carboxycyanamide, NC-NH-CO-OH.** Salts of this acid of the respective formulas, NC-N(Na)CO-ONa, or NC-N=C(ONa)<sub>2</sub>, C<sub>2</sub>O<sub>2</sub>N<sub>2</sub>K<sub>2</sub>, C<sub>2</sub>O<sub>2</sub>N<sub>2</sub>Ca.5H<sub>2</sub>O, C<sub>2</sub>O<sub>2</sub>N<sub>2</sub>Sr.xH<sub>2</sub>O and C<sub>2</sub>O<sub>2</sub>N<sub>2</sub>Ba.1½H<sub>2</sub>O, have been prepared as have also a sodium, potassium, silver and a basic copper salt of the ethyl ester, NC-NNa-CO-OC<sub>2</sub>H<sub>5</sub>, C<sub>2</sub>O<sub>2</sub>N<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>)K, C<sub>2</sub>O<sub>2</sub>N<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>)Ag and C<sub>2</sub>O<sub>2</sub>N<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>)CuOH. The ethyl ester is described as a strongly acid syrup. The free acid is unknown.

The formation of the disodium salt of cyancarbamic acid by the action of carbon dioxide on disodium cyanamide consists in the conversion of an ammonio unicarbonic acid salt into an aquo-ammonio dicarbonic acid salt, NCNNa<sub>2</sub> + CO<sub>2</sub> = NC-N=C(ONa)<sub>2</sub>. Inversely, when set free from its salts, cyancarbamic acid immediately decomposes to form cyanamide and carbon dioxide,



When disodium cyancarbamate is heated sodium cyanate is formed, NC-N(Na)CO-ONa = 2OCNNa, which is to say that by a process of intramolecular hydrolysis and ammonolysis each molecule of cyancarbamic acid is converted into two molecules of cyanic acid.

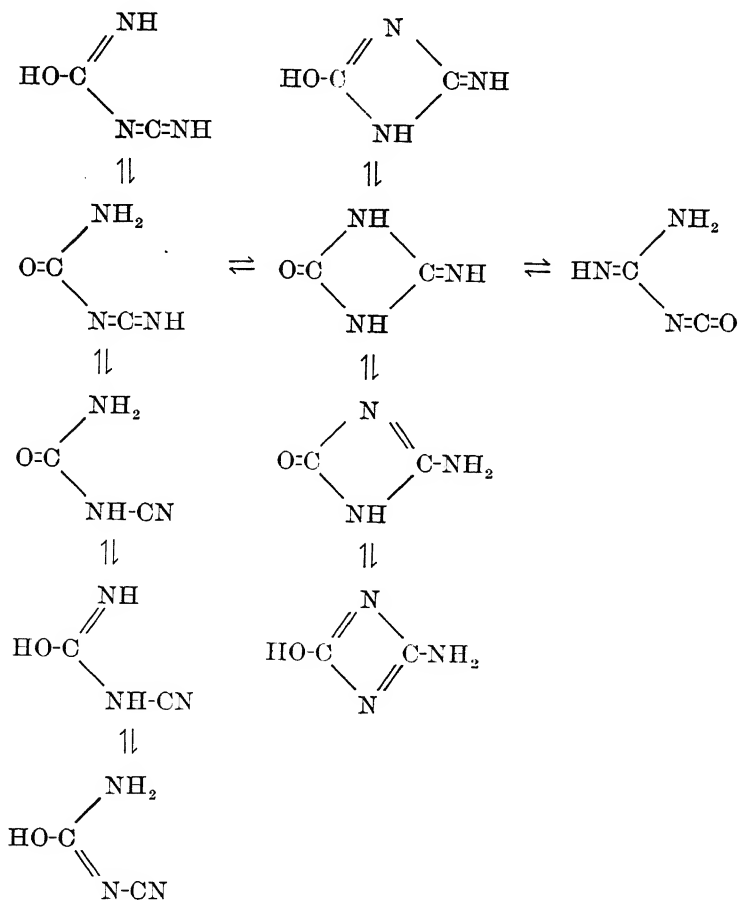
It is interesting to observe in this connection that cyandithiocarbamic acid, NC-NH-CS-SH, is known in the free state and in the form of metallic salts.

<sup>33</sup> Hofmann, *Ber.*, 4, 246 (1871); Snape, *J. Chem. Soc.*, 49, 254 (1886); G. E. P. Smith, Thesis, Stanford University, 1930.

9. Carbonylguanidine, Guanylisocyanate,  $\text{H}_2\text{N}-\text{C}(\text{NH})\text{N}=\text{CO}$ . The failure of attempts to prepare this compound may perhaps be explained on the assumption that it is a tautomer of cyanurea as explained in the following.

10. Cyanurea,  $\text{H}_2\text{N}-\text{CO}-\text{NH}-\text{CN}$ . The methods of formation of cyanurea and its behavior toward water, ammonia, hydrogen sulfide, acids and alkalis afford some interesting and at the same time simple examples of the large number of transformations which have been observed to characterize the aquo-ammono carbonic acids.

*Tautomerism of Cyanurea.* In the light of recent work conducted in this laboratory by Blair and Smith<sup>34</sup> it becomes reasonable to say that cyanurea is a tautomeric compound to which any one of the formulas given in the following scheme may be ascribed.

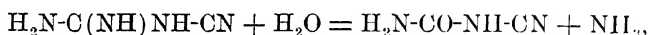


<sup>34</sup> Paper to be published.

Starting with the familiar formula,  $\text{H}_2\text{N-CO-NH-CN}$ , and ignoring the possibility of C-O-C linkages, nine further formulas for this aquo-ammono dicarbonic acid may be deduced by the same simple shifting of a hydrogen atom as is usually done in explanation of the tautomerism of urea,  $\text{OC}(\text{NH}_2)_2 \rightleftharpoons \text{HOCNH}(\text{NH}_2)$ , and of cyanic acid,  $\text{HNCO} \rightleftharpoons \text{NCOH}$ . In the interest of simplicity possible reciprocal transformations other than those given above are left unindicated. We shall go no further in the discussion of these tautomeric formulas other than to emphasize the reasonableness of Blair and Smith's arguments and to point out that carbonylguanidine, which has never been prepared, appears as a tautomeric form of cyanurea.

*Formation.* Of the three methods for the preparation of cyanurea the one, accomplished by the interaction of potassium cyanate and cyanamide in water solution,  $\text{HN=CO} + \text{H}_2\text{N-CN} = \text{H}_2\text{N-CO-NH-CN}$ , consists in the coalescence of an aquo-ammono unicarbonic acid with an ammono unicarbonic acid to form a mixed aquo-ammono dicarbonic acid. The reaction involved is in principle the same as that which takes place when cyanic acid is ammonated to urea, when cyanic acid dimerizes to dicyanic acid, or when cyanamide is converted into dicyandiamide.

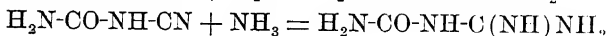
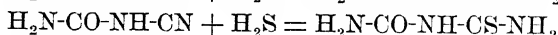
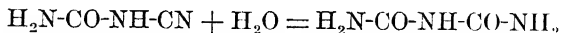
The second method for the preparation of cyanurea by the action of barium hydroxide on dicyandiamide in water solution involves the partial hydrolysis of an ammono dicarbonic acid to form an aquo-ammono dicarbonic acid as represented by the equation,



or by any one of several others which may be written.

According to Short<sup>35</sup> cyanurea is formed by the action of aqueous hydrochloric acid on the silver salt of dicyanimide. Represented by the equation,  $\text{NC-NH-CN} + \text{H}_2\text{O} = \text{NC-NH-CO-NH}_2$ , the reaction consists in the hydration of an ammono dicarbonic acid to an aquo-ammono dicarbonic acid.

*Reactions.* The three equations,

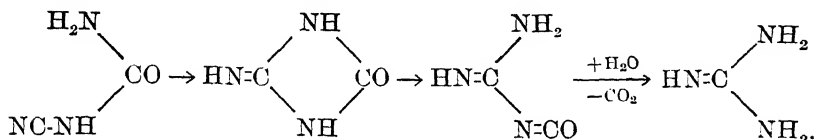


represent the action of water, hydrogen sulfide and ammonia on cyanurea to form biuret, monothioibiuret and dicyandiamidine re-

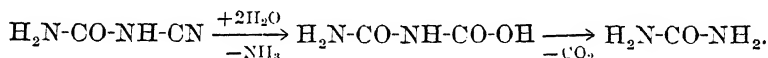
<sup>35</sup> Short, *Chem. News*, 126, 100 (1923); Madelung and Kern, *Ann. Chem.*, 427, 25 (1922).

spectively. Biuret is formed when cyanurea is warmed with dilute sulfuric acid, monothioibiuret when cyanurea is heated with a water solution of ammonium sulfide while the silver salt of cyanurea is converted into dicyandiamidine when heated with a water solution of ammonium chloride. In each case the aquo-ammono dicarbonic acid is converted into a more highly solvated carbonic acid.

Smith<sup>36</sup> found that in addition to biuret small amounts of urea and guanidine are formed when cyanurea is digested with warm dilute sulfuric acid. The presence of guanidine among the reaction products is explained by Smith on the assumption that a tautomeric form of cyanurea, namely carbonyl guanidine (third formula below) undergoes hydrolysis in accordance with the equation,



The formation of urea probably takes place in accordance with the equation,



Under the action of hot alcoholic potassium hydroxide solution cyanurea breaks apart to form potassium cyanate and cyanamide,  $\text{H}_2\text{N-CO-NH-CN} = \text{H}_2\text{N-CN} + \text{HN-CO}$ .

*Metallic Salts.* Cyanurea is a moderately strong acid of which a potassium salt,  $\text{C}_2\text{H}_2\text{ON}_3\text{K}$ , a sodium salt,  $\text{C}_2\text{H}_2\text{ON}_3\text{Na}$ , two copper salts,  $(\text{C}_2\text{H}_2\text{ON}_3)_2\text{Cu} \cdot 4\text{H}_2\text{O}$  and  $\text{C}_2\text{HON}_3\text{Cu} \cdot 2\text{H}_2\text{O}$ , a silver salt,  $\text{C}_2\text{H}_2\text{ON}_3\text{Ag}$ , and a barium salt,  $(\text{C}_2\text{H}_2\text{ON}_3)_2\text{Ba} \cdot 3\text{H}_2\text{O}$ , have been prepared. Using liquid ammonia as solvent in which to carry on the reactions involved Smith<sup>36</sup> prepared the three potassium salts of cyanurea represented by the formulas,  $\text{C}_2\text{H}_2\text{ON}_3\text{K}$ ,  $\text{C}_2\text{HON}_3\text{K}_2$  and  $\text{C}_2\text{ON}_3\text{K}_3$ .

Certain esters of cyanurea are possessed of distinct acid properties as is shown by the existence of a sodium salt,  $\text{C}_2\text{HON}_3(\text{C}_2\text{H}_5)\text{Na}$ , a silver salt,  $\text{C}_2\text{HON}_3(\text{C}_2\text{H}_5)\text{Ag}$ , and a copper salt,  $[\text{C}_2\text{HON}_3(\text{C}_2\text{H}_5)]_2\text{Cu} \cdot 5\text{H}_2\text{O}$ , of N-ethylcyanurea and of a sodium salt of O-ethylcyanurea,  $\text{C}_2\text{H}_5\text{O-C}(\text{NNa})\text{NH-CN}$ .<sup>37</sup>

By the action of potassium amide on N-phenylcyanurea in liquid ammonia solution Smith<sup>36</sup> prepared the potassium salt represented by the formula,  $\text{C}_6\text{H}_5\text{NH-CO-NK-CN}$ .

<sup>36</sup> G. E. P. Smith, Thesis, Stanford University, 1930.

<sup>37</sup> Madelung and Kern, *Ann. Chem.*, 427, 22 (1922).

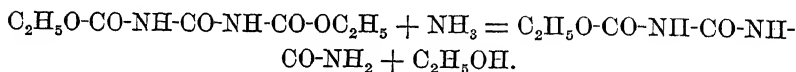


## AQUO-AMMONO POLYCARBONIC ACIDS

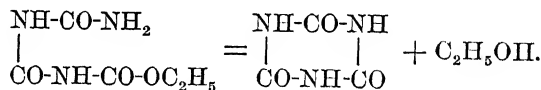
Compounds in considerable number are on record containing the skeletal groups, C-N-C-N-C, C-N-C-N-C-N-C and C-N-C-N-C-N-C-N-C, which are to be looked upon as polycarbonic acids. Certain of these compounds are known in the free state, others in the form of esters, some of them in the form of salts, some as ester-salts. Examples of these polycarbonic acids are the following.

1. Carbonyldicarbamic Acid, Symmetrical Dicarboxylurea,  $\text{HO-CO-NH-CO-NH-CO-OH}$ , is not known in the free state nor in the form of metallic salts. Sodium and silver salts of the diethyl ester known as carbonyldiurethane,  $\text{C}_2\text{H}_5\text{O-CO-NH-CO-NH-CO-OC}_2\text{H}_5$ , have been prepared.<sup>38</sup>

2. Carboxylbiuret,  $\text{H}_2\text{N-CO-NH-CO-NH-CO-OH}$ , is unknown in the free state. An O-ethyl ester has been obtained by the ammonolytic action of liquid ammonia on carbonyldiurethane as represented by the equation,



This ester readily loses alcohol to form cyanuric acid,



It may be said of this reaction that the ester of a straight chain aquo-ammono tricarbonic acid undergoes intramolecular ammonolysis to form a cyclic aquo-ammono tricarbonic and ethyl alcohol.

A disodium salt,  $\text{C}_{11}\text{H}_{11}\text{O}_4\text{N}_3\text{Na}_2$ , and a disilver salt,  $\text{C}_{11}\text{H}_{11}\text{O}_4\text{N}_3\text{Ag}_2$ , of the phenyl ethyl ester,  $\text{C}_6\text{H}_5\text{NH-CO-NH-CO-NH-CO-OC}_2\text{H}_5$ , of this aquo-ammono tricarbonic acid have been prepared.<sup>38</sup>

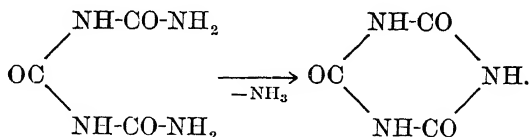
3. Symmetrical Dicarboxylguanidine,  $\text{HO-CO-NH-C(NH)NH-CO-OH}$ , is known only in the form of its O-O'-diethyl ester. No metallic salts either of the acid or of the acid ester have been prepared.

4. Carbonyldiurea, Triuret,  $\text{H}_2\text{N-CO-NH-CO-NH-CO-NH}_2$ . A disilver salt,  $\text{C}_3\text{H}_4\text{O}_3\text{N}_4\text{Ag}_2$ , a basic mercuric salt,  $\text{C}_3\text{H}_5\text{O}_3\text{N}_4\text{HgOH}$ , a monopotassium salt,  $\text{C}_3\text{H}_5\text{O}_3\text{N}_4\text{K}$ , and a dipotassium salt,  $\text{C}_3\text{H}_4\text{O}_3\text{N}_4\text{K}_2$ , of triuret have been prepared; the latter two salts by the ac-

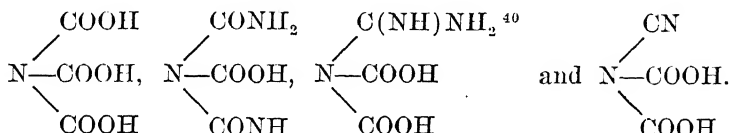
<sup>38</sup> Dains, Greider and Kidwell, *J. Am. Chem. Soc.*, **41**, 1004 (1919).

tion of potassium amide on triuret in liquid ammonia solution.<sup>39</sup>

It is interesting to note that triuret is readily converted into cyanuric acid. Heated to a moderate temperature it loses ammonia and passes over into this cyclic aquo-ammono carbonic acid,



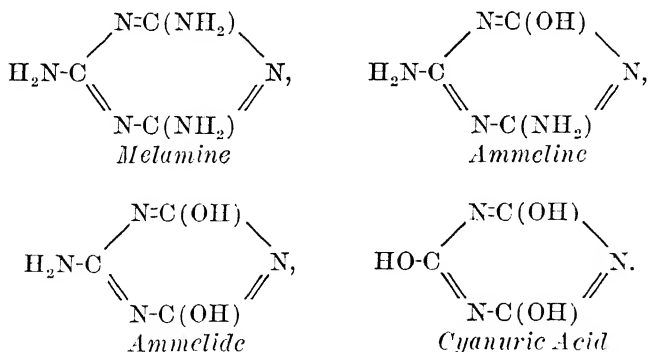
**Carbonic Acids Containing Tertiary Nitrogen.** Of the sixteen theoretically possible tricarbonic acids containing tertiary nitrogen the following are known and they only in the forms of esters,



#### CYCLIC AQUO-AMMONO CARBONIC ACIDS

Just as cyanamide and dicyanamide, two ammono carbonic acids, readily polymerize to the two cyclic ammono carbonic acids known respectively as melamine and tricyanmelamine, so cyanic acid, an aquo-ammono carbonic acid, even more readily polymerizes to cyanuric acid. Clearly the latter reaction may be said to result in the formation of a cyclic aquo-ammono tricarbonic acid.

Occupying positions between melamine and cyanuric acid as represented by the following formulas,



<sup>39</sup> Blair, *J. Am. Chem. Soc.*, **48**, 101 (1926).

<sup>40</sup> Pinck and Blair, *J. Am. Chem. Soc.*, **49**, 514 (1927).

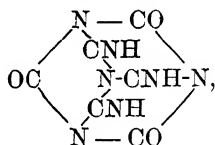
are two further cyclic aquo-ammono tricarbonic acids known respectively as ammeline and ammelide. Each of these four cyclic acids may be represented by two tautomeric formulas.

1. **Ammeline**,  $C_3H_5ON_5$ . Esters of ammeline as well as of thioammeline are known. No metallic salts of ammeline have been prepared, though the existence of a mono- and a di-silver salt of thioammeline,  $C_3H_4N_5SAg$  and  $C_3H_3N_5S_2Ag_2$ , together with the fact that salts of the presumably much weaker acid, melamine, have been obtained by working with liquid ammonia as a solvent makes it probable that metallic salts of ammeline are capable of existence.

2. **Ammelide**, **Melanurenic Acid**,  $C_3H_4O_2N_4$ . A considerable number of salts and esters of this compound have been prepared. Esters of both the normal and iso acids, as well as salts and esters of dithioammelide are known.

3. **Cyanuric Acid**,  $C_3H_3O_3N_3$ . Many alkyl and aryl derivatives of cyanuric acid are known both in the form of O-esters and N-esters. It is interesting to note that the mercuric salt has been found to exist in two isomeric forms which Hantzsch<sup>41</sup> explains on the assumption that the one is a salt of the normal acid and the other of the iso acid.

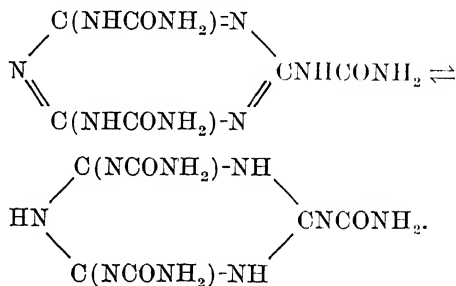
4. **Cyameluric Acid**,  $C_6H_3O_8N_7$ ,



is an aquo-ammono hexacarbonic acid to which, in view of the established structure of hexamethylenetetramine, the above formula, or some modification thereof, may reasonably be ascribed.

Salts of cyameluric acid formulated as follows have been prepared:  $C_6O_8N_7K_3 \cdot 2H_2O$ ,  $C_6H_2O_8N_7K \cdot 2H_2O$ ,  $(C_6O_8N_7)_2Ba_3 \cdot H_2O$ , and  $C_6O_8N_7Ag_3$ .

5. **Tricyanurea**, **Cyanurtriureide**,



<sup>41</sup> Hantzsch, *Ber.*, 35, 2717 (1902).

This aquo-ammono hexacarbonic acid was first recognized by Hantzsch as one of the products formed by heating urea. It is also formed when biguanide is heated and by the action of urea of cyanuric acid or of cyanuric bromide.<sup>42</sup>

More recently Smith<sup>43</sup> has shown that cyanurea in water solution at 90° gradually polymerizes to its trimeric form.

A sodium salt,  $C_6H_6O_3N_9Na_3 \cdot 5NH_3$ , and an unanalyzed mercuric salt of this cyclic carbonic acid have been prepared.

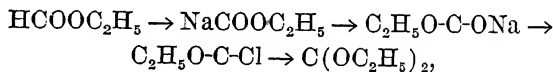
<sup>42</sup> Hantzsch, Bauer and Hofmann [*Ber.*, **38**, 1010 (1905)]. It may be noted that according to Werner [*J. Chem. Soc.*, **103**, 2275 (1913)] the compound reported by Hantzsch, Bauer and Hofmann as tricyanurea was ammelide.

<sup>43</sup> G. E. P. Smith, Thesis, Stanford University, 1930.

## CHAPTER XII.

### AMMONO CARBONOUS ACID.

When the well-known tautomeric properties of nitrous acid, phosphorous acid and sulfurous acid, represented respectively as follows,  $\text{HNO}_2$ ,  $\text{HONO}$ ,  $\text{HPO}(\text{OH})_2 \rightleftharpoons \text{P}(\text{OH})_3$  and  $\text{HSO}_2\text{OH} \rightleftharpoons \text{OS}(\text{OH})_2$ , are recalled, one is led to inquire whether possibly there is any evidence of a similar tautomeric behavior on the part of formic acid, that is to say whether formic acid shows any of the properties of a carbonous acid. Excepting Baly's speculations to the effect that the hydration of activated carbon monoxide to formic acid follows the course,  $\text{CO} \xrightarrow{+\text{H}_2\text{O}} \text{C}(\text{OH})_2 \rightarrow \text{HCOOH}$ ,<sup>1</sup> and Scheibler's observations on the preparation of diethyl carbonite (Kohlenoxid-diaethyl-acetal) by means of reactions summarized by the scheme,



little is known concerning possible tautomeric properties of formic acid.<sup>2</sup>

On the other hand it is proposed to show in the following pages that hydrocyanic acid, in so far as it may be represented by the formula,  $\text{HCN}$ , is a carbonous acid of the nitrogen system, that its metallic derivatives are ammonocarbonites and that the isonitriles are ammono carbonous acid esters.

**Ammono Carbonous Acid,  $\text{H} \cdot \text{N} \vdash \text{C}$ .** The formulas,  $\text{C}(\text{OH})_2$  and  $\text{C}(\text{NH}_2)_2$ , in which the carbon atom is assumed to be dipositive, may be written to represent respectively an aquo carbonous acid and an ammono carbonous acid. The removal of the elements of water from the hypothetical compound of the first formula leaves carbon monoxide which thus appears as carbonous anhydride. The analogous loss of ammonia from the unknown ammono carbonous acid,  $\text{C}(\text{NH}_2)_2$ , and from formamidine,  $\text{HC}(\text{NH})\text{NH}_2$ , which is an ammono formic acid leaves hydrocyanic acid represented in the one case by the formula,  $\text{HCN}$ , in the other by  $\text{HCN}$ . The first formula

<sup>1</sup> Baly, Heilbronn and Hudson, *J. Chem. Soc.*, 121, 1080 (1922).

<sup>2</sup> Scheibler, *Ber.*, 59, 1022 (1925), 60, 554 (1927). A number of chemists, including Dr. Dennistoun Wood of this laboratory [Thesis, Stanford University, 1930], has been unable to confirm Scheibler's results.

is that of an ammono carbonous acid, the second that of formic anammonide.<sup>3</sup>

Hydrocyanic acid is a typical tautomeric compound which in the liquid form consists of a mixture of much formic anammonide and very little ammono carbonous acid.<sup>4</sup>

**Formation of Hydrocyanic Acid and the Alkali Metal Cyanides.** From the large number of procedures which have lent themselves to the preparation of hydrocyanic acid and its salts the following have been selected for consideration here.

1. *The Action of Ammonia or of a Mixture of Nitrogen and Hydrogen on Carbon.* Neither a carbonous nitride nor a carbonic nitride is formed when carbon is heated in an atmosphere of nitrogen. When however carbon is exposed to a high temperature in contact with a mixture of nitrogen and hydrogen, or with ammonia, hydrocyanic acid is among the products formed. When carbon is heated in the presence of an alkali metal and nitrogen a metallic cyanide is formed. The formation of hydrocyanic acid and of alkali cyanide may reasonably be interpreted as consisting in the nitridation of carbon and hydrogen to ammono carbonous acid in the one case and of carbon and alkali metal to an ammonocarbonite in the other.

2. *The Action of Sodium Amide on Carbon.* It has been found that sodium amide at a temperature of 350° to 400° dissolves carbon to form disodium cyanamide and that at higher temperatures disodium cyanamide, in the presence of carbon, undergoes reduction to sodium cyanide.<sup>5</sup> The reactions are represented by the equations,  $2\text{NaNH}_2 + \text{C} = \text{Na}_2\text{CN}_2 + 2\text{H}_2$  and  $\text{Na}_2\text{NCN} + \text{C} = 2\text{NaNC}$ , and are significant in the present connection for the reason that the one involves the nitridation of carbon to an ammonocarbonate and the other the reduction of an ammonocarbonate to an ammonocarbonite.

3. *Reduction of Ammonocarbonates to Ammonocarbonites.* The reduction of sodium cyanamide has already been considered. The ammono carbonic acid known as dicyandiamide,  $\text{H}_4\text{C}_2\text{N}_4$ , yields sodium cyanide when heated with sodium hydroxide and carbon. The sodium ammonocarbonate of the formula,  $\text{Na}_3\text{C}_6\text{N}_9$ , known as tri-sodium tricyanmelamine, is reduced to sodium cyanide, with the simultaneous formation of cyanogen and nitrogen, simply by heating to redness, or with the formation of sodium cyanide and nitrogen, by heating in the presence of metallic sodium. Liebig's potassium

<sup>3</sup> Franklin, *J. Phys. Chem.*, 27, 167 (1923).

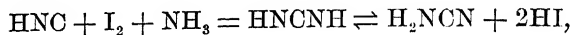
<sup>4</sup> Meyer and Hopff, *Ber.*, 54, 1709 (1921); Usherwood, *J. Chem. Soc.*, 121, 1604 (1922).

<sup>5</sup> Castner, *Z. anorg. Chem.*, 10, 288 (1897), *Chem. Zentr.*, 1904, I, 411.

melonate,  $K_3C_9N_{13}$ , which is another ammonocarbonate, yields potassium cyanide when heated.<sup>7</sup>

4. *Reduction of Potassium Cyanate and Potassium Thiocyanate.* As is well known both these salts on reduction yield potassium cyanide. It may be said that potassium ammonocarbonite is formed by the reduction, in the one case of an aquo-ammono-carbonate, in the other of a thio-ammono-carbonate.

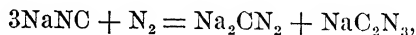
**Nitridation of Hydrocyanic Acid.** Strain<sup>8</sup> has shown that hydrocyanic acid in liquid ammonia solution is converted into a mixture of cyanamide and guanidine when treated with iodine. The reaction involved in the formation of cyanamide,



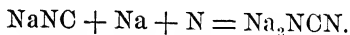
may be explained as consisting in the nitridation of ammono carbonous acid to an ammono carbonic acid and the simultaneous reduction of iodine to hydriodic acid. Alternately one may of course represent hydrocyanic acid by the formula,  $HCN$ , and say that iodine nitridizes formic anammonide to an ammono carbonic acid. It is known that guanidine is formed by the ammonation of cyanamide.

It has also been shown in this laboratory that solid bromine added to a cold liquid ammonia solution of potassium cyanide gives a good yield of cyanamide.

**The Nitridation of Sodium Ammonocarbonite.** 1. Sodium cyanide may be nitridized to disodium cyanamide just as it may be oxidized to sodium cyanate or sulfidized to sodium thiocyanate but not, as it appears, by simply heating in the presence of nitrogen. Efforts made in this laboratory to nitridize sodium cyanide by heating the cyanide at varying high temperatures in an atmosphere of nitrogen—alone and in the presence of iron and platinum acting as possible catalysts—have not met with success. These experiments were undertaken on the presumption that possibly sodium cyanide might be nitridized in accordance with the equation,



to form a mixture of disodium cyanamide and sodium dicyanimide. However the nitridation of sodium cyanide is easily accomplished when, in the presence of metallic sodium, it is heated in an atmosphere of nitrogen. In accordance with the equation,

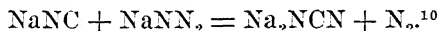


<sup>7</sup> Franklin, *J. Phys. Chem.*, 27, 176 (1923).

<sup>8</sup> Strain, Thesis, Stanford University, 1927.

Sodium ammonocarbonite and metallic sodium are nitridized to form sodium ammonocarbonate.<sup>9</sup>

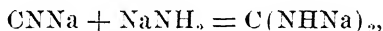
2. When sodium azide is carefully added to fused sodium cyanide the latter salt is converted into disodium cyanamide,



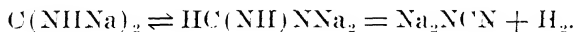
In Chapter 14 it is shown that hydrazoic acid is to be looked upon as a nitric acid of the nitrogen system. This being the case its sodium salt should act as a nitridizing agent just as ordinary sodium nitrate acts as an oxidizing agent.

3. A fair yield of trisodium tricyanmelamine is obtained by heating a mixture of sodium cyanide and mercuric cyanide.<sup>11</sup> Cyanogen, formed by the decomposition of mercuric cyanide, nitridizes sodium cyanide in a manner which may be represented by the equation,  $\text{NaNC} + \text{C}_2\text{N}_2 = \text{NaN}(\text{CN})_2 + \text{C}$ , to sodium dicyanimide. At a temperature of low redness this ammonocarbonate of sodium undergoes polymerization to trisodium tricyanmelamine (p. 104). The nature of the simultaneously formed reduction product has not been determined. It is represented in the equation as carbon. Dicyanimide and tricyanmelamine are ammono carbonic acids.

4. Sodium cyanide dissolves in fused sodium amide without obvious evidence of chemical action. When the fused mixture is heated to 400° disodium cyanamide and hydrogen are formed as represented by the equation,  $\text{NaNC} + \text{NaNH}_2 = \text{Na}_2\text{NCN} + \text{H}_2^{12}$ . Probably, in accordance with the equation,



a disodium salt of ortho ammono carbonous acid, or perhaps of formamidine,  $\text{HC}(\text{NH})\text{NNa}_2$ , is formed which at the higher temperature decomposes into sodium cyanamide and hydrogen,



It will be recalled that analogously sodium formate yields sodium carbonate and hydrogen when heated with sodium hydroxide,



<sup>9</sup> Drechsel, *J. prakt. Chem.*, [2] 21, 81 (1880).

<sup>10</sup> Franklin, *J. Phys. Chem.*, 27, 167 (1923).

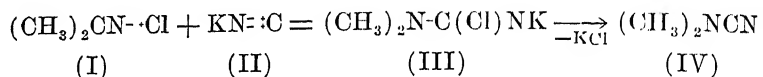
<sup>11</sup> Franklin, *J. Am. Chem. Soc.*, 44, 499 (1922).

<sup>12</sup> *Chem. Zentr.*, 1901, II, 1100.



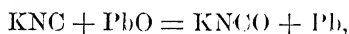
**Intramolecular Nitridation and Reduction of Barium Ammonocarbonite.** Drechsel<sup>13</sup> observed that barium cyanamide is formed when barium cyanide is heated out of contact with atmospheric air. The reaction involved, which may be represented by the equation  $\text{Ba}(\text{CN})_2 = \text{BaCN}_2 + \text{C}$ , is interesting as an example of a Cannizzaro-like reaction. Of the two carbonous acid groups contained in the molecule of barium cyanide, the one is nitridized to an ammonio carbonic acid radical the other simultaneously undergoing reduction to elementary carbon.

**The Interaction of Potassium Cyanide and Dimethylchloramine.** Dimethylcyanamide and potassium chloride are formed when potassium cyanide is added to an alcoholic solution of dimethylchloramine.<sup>14</sup> The reactions involved may be represented by the equation,



and interpreted as consisting first in the nitridizing action of the hypochlorous acid chlorine contained in the dimethyl ammonio hypochlorite (I) on potassium ammonocarbonite (II) to form an hypothetical compound (III) which is at the same time a potassium ammonocarbonate, a carbonic acid chloride and a carbonic acid ester and, second, the dissociation of this assumedly unstable compound to form the dimethyl ammonocarbonate (IV) and potassium chloride.

**Oxidation of Potassium Ammonocarbonite.** As is familiarly known potassium cyanide is easily oxidized to potassium cyanate. Since potassium cyanate is a mixed aquo-ammonio-carbonate of potassium it is clear that the reaction which takes place when for instance lead oxide acts on fused potassium cyanide,



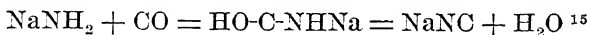
consists in the oxidation of an ammonocarbonite to an aquo-ammonio-carbonate.

**Carbon Monoxide a Carbonous Anhydride.** Carbon monoxide may be looked upon as the anhydride of an unknown aquo carbonous acid though of course such a view receives little or no support from its behavior toward aquo bases. The action of carbon monoxide on sodium amide however is in harmony with this assumption

<sup>13</sup> Drechsel, *J. prakt. Chem.*, [2] 21, 83 (1880); Askew and Grade, *Z. Elektrochem.*, 28, 130 (1922).

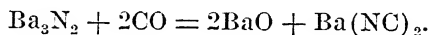
<sup>14</sup> Berg, *Ann. chim.*, [7] 3, 352 (1894).

since it is absorbed readily by fused sodium amide to form sodium cyanide in accordance with the equation,



This equation may be read as representing the action of carbonous anhydride on a sodium ammono base to form an ammonocarbonite of sodium. Carbon monoxide acts in a similar manner on fused potassium amide to form potassium cyanide.<sup>16</sup>

Another reaction closely resembling the foregoing, due to Maquenne<sup>17</sup> is represented by the equation,



Barium nitride, which is the nitrogen analog of barium oxide, reacts with carbon monoxide to form barium oxide and barium ammonocarbonite. Again noting the fact that metallic aquocarbonites are unknown one is prepared to find that one of the products of Maquenne's reaction to be barium oxide instead of a barium aquocarbonite.

**Esters of Ammono Carbonous Acid.** As is well known the alkyl and aryl derivatives of hydrocyanic acid exist in two isomeric forms, namely as the nitriles, RCN, which are carbazylic acid anammonides, and the isocyanides or carbylamines, RNC, which are esters of ammono carbonous acid.

*Ammonolysis of Ethyl Isocyanide.* Regarded as esters of an ammono carbonous acid the isocyanides should be susceptible to ammonolytic decomposition to form ammono alcohols and hydrocyanic acid just as aquo esters in general upon hydrolysis yield aquo alcohols and aquo acids. As a matter of fact such an ammonolytic decomposition of ethyl isocyanide has been accomplished by warming the ester in contact with either sodium amide or potassium amide in the absence of a solvent and also by dissolving the ester in liquid ammonia, adding an equivalent quantity of potassium amide and heating the mixture for a time at a temperature of 80°. The reaction products consist of a limited amount of tarry material together with abundant yields of hydrocyanic acid and ethylamine. The reaction takes place in accordance with the equation,  $\text{C}_2\text{H}_5\text{NC} + \text{KNH}_2 = \text{C}_2\text{H}_5\text{NH}_2 + \text{KNC}$ , which represents the ammonolysis of ethyl ammonocarbonite to an ammono ethyl alcohol and potassium ammonocarbonate.<sup>18</sup> The analogy between

<sup>15</sup> Beilstein and Gunther, *Ann. Chem.*, **108**, 93 (1857); cf. Stähler, *Ber.*, **47**, 586, 912 (1914).

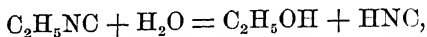
<sup>16</sup> Conroy, *J. Soc. Chem. Ind.*, **15**, 9 (1906).

<sup>17</sup> Maquenne, *Ann. chim. phys.*, [6] **29**, 223 (1893).

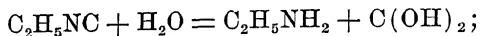
<sup>18</sup> Franklin, *J. Phys. Chem.*, **27**, 177 (1923).

this reaction and the familiar saponification of an ordinary ester so obvious as to require no further elucidation.

Looked upon as the ethyl ester of ammono carbonous acid ethyl isocyanide undergoing hydrolysis instead of ammonolysis might be expected to yield either ethyl alcohol and hydrocyanic acid,



or perhaps rather, ethylamine and aquo carbonous acid,



or, since aquo carbonous acid is incapable of existence, its isomer formic acid. As is familiarly known the hydrolytic decomposition of ethyl isocyanide follows the latter course.

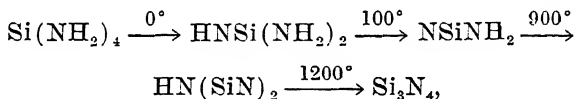
*Oxidation of Methyl Ammonocarbonite.* Another reaction in support of the view that methyl isocyanide is an ammonocarbonite is due to Gautier.<sup>19</sup> Warmed gently in contact with mercuric oxide methyl isocyanide is oxidized to methyl isocyanate. The equation,  $\text{CH}_3\text{NC} + \text{HgO} = \text{CH}_3\text{NCO} + \text{Hg}$ , in accordance with which the reaction takes place, represents the oxidation of an ester of ammono carbonous acid to the corresponding N-ester of a mixed aquo-ammono carbonic acid. Similarly Gautier showed that methyl isocyanide is sulfidized by the action of sulfur at 130° to methyl isothiocyanate, which is an ammono methyl ester of a thio-ammonocarbonic acid.

<sup>19</sup> Gautier, *Ann. chim. phys.*, [4] 17, 128 (1869).

## CHAPTER XIII.

### AMIDES AND IMIDES OF SILICON, TITANIUM, GERMANIUM, ZIRCONIUM, TIN AND THORIUM.

**Ammono Silicic Acids, Silicon Tetramide,  $\text{Si}(\text{NH}_2)_4$ , Silicoguanidine,  $\text{HN}=\text{Si}(\text{NH}_2)_2$ , Silicocyanamide,  $\text{H}_2\text{N}-\text{SiN}$ , and Silicam (Silicodicyanamide),  $\text{HN}(\text{SiN})_2$ .** When treated with liquid ammonia at  $-50^\circ$  silicon tetrachloride is ammonolyzed in accordance with the equation,  $\text{SiCl}_4 + 4\text{NH}_3 = \text{Si}(\text{NH}_2)_4 + 4\text{HCl}$ , to an ortho-ammono silicic acid known as silicon tetramide.<sup>1</sup> This compound loses ammonia stepwise at the temperatures indicated in the scheme,



being thereby converted finally into silicic anammonide. All four of these ammono silicic acids are insoluble in liquid ammonia. Silicoguanidine and silicocyanamide are readily hydrolyzed by the action of water, silicam very slowly.

**Potassium Ammonosilicate.** An insoluble, non-crystalline product, in composition approximating the formula,  $\text{SiH}_7\text{N}_4\text{K}$ , has been obtained by the action of an excess of potassium amide on the precipitate formed by the action of liquid ammonia on silicon tetrabromide.<sup>2</sup>

Whether the compound is a potassium salt of silicon amide,  $\text{KNHSi}(\text{NH}_2)_3$ , of silicoguanidine,  $\text{KNSi}(\text{NH}_2)_2\cdot\text{NH}_3$ , or of silicon imide,  $\text{KNSiNH}_2\text{NH}_3$ , is an open question.

Petersen<sup>3</sup> has shown that silicon and aluminum in silicate minerals may be determined quantitatively by fusing the finely powdered mineral with sodium amide in an atmosphere of ammonia, hydrolyzing the melt with water, acidifying with hydrochloric acid and then proceeding in the usual manner for the recovery of silica and alumina.

<sup>1</sup> Lengfeld, *Am. Chem. J.*, **21**, 531 (1899); Vigoroux and Hugot, *Compt. rend.*, **136**, 1670 (1903); Blix and Wirbelauer, *Ber.*, **36**, 4220 (1903); according to Stock and Zeidler [*Ber.*, **56**, 986 (1923)] silicoguanidine is formed by the action of liquid ammonia on silicon tetrachloride.

<sup>2</sup> Franklin and Hine, *J. Am. Chem. Soc.*, **34**, 1497 (1912).

<sup>3</sup> Petersen and Bergstrom, *Ind. Eng. Chem., Analytical Ed.*, **6**, 136 (1934).

Some of the results obtained by Petersen are reproduced in Table 7. In the columns under I are given the silica and alumina content of the several minerals which were opened by fusion with sodium amide. The check data given in the columns under II were obtained by the ordinary sodium carbonate-potassium carbonate fusion method.

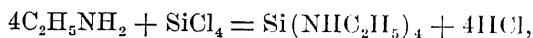
TABLE 7.—*Analyses of Minerals by Fusion with Sodium Amide in an Atmosphere of Ammonia.*

	I		II	
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>
	Per Cent			
Feldspar .....	65.7, 65.5	18.8	65.5	19.0
Serpentine .....	35.4, 35.1	....	35.2	....
Soapstone .....	36.5, 36.7, 36.5, 36.5	18.9	36.7	19.0
Calamine .....	29.0, 28.9	....	29.0	....
Soda glass .....	73.9, 74.1	....	74.1	....
Lead glass .....	65.3, 65.4	....	65.4	....
Pyrex glass .....	80.2, 80.1	....	80.1	....
Glass sand .....	99.3, 99.3	....	99.3	....

The hypothesis upon which this work was undertaken is to the effect that just as fused sodium hydroxide dissolves aluminum silicates to form sodium aluminates and sodium silicates so sodium amide, the sodium base of the ammonia system, in dissolving aluminum silicate should form a melt containing a mixture of sodium aquoaluminates, sodium ammonoaluminates, sodium aquosilicates and sodium ammonosilicates; and that, furthermore, the mixed silicates thus formed should undergo hydrolytic decomposition in the presence of water to yield the same products as are obtained when the ordinary sodium carbonate melt is treated with water. The results obtained justify these speculations which led to Peterson's work.

*Esters of Ortho Ammono Silicic Acid.* Silicon tetrachloride has been observed to act with ethylamine, with aniline and with ortho and para-toluidine to form compounds represented by the respective formulas,  $\text{Si}(\text{NHC}_2\text{H}_5)_4$ ,  $\text{Si}(\text{NHC}_6\text{H}_5)_4$  and  $\text{Si}(\text{NHC}_6\text{H}_4(\text{CH}_3))_4$ .<sup>4</sup>

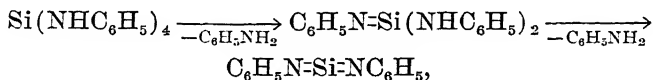
The reaction between silicon tetrachloride and ethylamine for example takes place in accordance with the equation,



which may be read as representing the action of a silicic acid chloride on an ammono ethyl alcohol to form an ammono silicic acid ester.

<sup>4</sup> Lengfeld, *Am. Chem. J.*, **21**, 536 (1899); Reynolds, *J. Chem. Soc.*, **55**, 47 (1889); **77**, 836 (1900); **87**, 1870 (1905).

According to Reynolds, triphenyl silicoguanidine and silico diphenyldiimide are successively formed as represented by the scheme,



when silicic acid tetranilide is heated in a current of hydrogen. These compounds are to be looked upon as phenyl esters of the silicon analogs of the ammono carbonic acids represented by the respective formulas,  $\text{C}(\text{NH}_2)_4$ ,  $\text{HNC}(\text{NH}_2)_2$  and  $\text{NCNH}_2 \rightleftharpoons \text{NN}=\text{C}=\text{NH}$ . In the presence of water all these ammono silicic acid esters are hydrolyzed to aquo silicic acid and the respective amines.

It is worth while in this connection to recall the existence of silicon nitrogen compounds represented by the following formulas. (1)  $(\text{SiH}_3)_2\text{NH}$ , (2)  $(\text{SiH}_3)_3\text{N}$ , (3)  $\text{SiH}_2=\text{NH}$ , (4)  $\text{HSi}(\text{NHC}_6\text{H}_5)_3$ , (5)  $\text{HSi}(\text{NH})\text{-NH}(\text{NH})\text{SiH}$ , (6)  $\text{HSiN} \rightleftharpoons \text{SiNH}$ , (7)  $\text{H}_2\text{N}(\text{NH})\text{-Si-Si}(\text{NH})\text{NH}_2$ , (8)  $\text{N}=\text{Si-Si}(\text{NH})\text{NH}_2$ , and (9)  $\text{SiN}$ , and to point out that silicodimethylamine (1) and silicotrimethylamine (2) are to be regarded respectively as an ammono-silico methyl alcohol and an ammono-silico methyl ether. Formula (3) represents the silicon analog of methyleneimine. Formula (4) represents a triphenyl ester of ortho-ammono silicoformic acid, (5) an ammono silicoformic acid, (6) either a silico formic anammonide or an ammono silicious acid, (7) and (8) ammono-silico oxalic acids. Formula (9) if written  $\text{Si}_2\text{N}_2$  represents silico cyanogen, which is the anammonide of silico oxalic acid.

Silicodimethylamine (1) and silico trimethylamine (2) are volatile monomolecular liquids. Silico methyleneimine (3) has been obtained as an associated liquid which rapidly goes over into a solid polymer. The other compounds, excepting (4), are known only in their highly polymerized forms.<sup>5</sup>

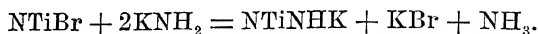
**Ammono Titanic Acids.** *Titanium Tetramide*,  $\text{Ti}(\text{NH}_2)_4$ , *Titanocyanamide*,  $\text{H}_2\text{NTiN}$ . Blix and Wirbelauer<sup>6</sup> tell us that titanium tetramide,  $\text{Ti}(\text{NH}_2)_4$ , is formed by the action of liquid ammonia on titanium chloride and that the tetramide when heated is converted into titanium diimide,  $\text{Ti}(\text{NH})_2$ . Both these compounds are to be regarded as ammono titanic acids.

*Potassium Ammonotitanate*,  $\text{N}^-\text{Ti-N}^+\text{HK}$ ,  $\text{HN}=\text{Ti-NK}$ . Titanium nitride-bromide,  $\text{NTiBr}$ , in contact with a liquid ammonia solution of potassium amide in excess is slowly converted into a brick-red powder approximately of the composition represented by the above

<sup>5</sup> Stock and Zeidler, *Ber.*, 56, 986 (1923); Ruff, *Ber.*, 41, 3738, 3743 (1908); Schwarz and Sexauer, *Ber.*, 59, 333 (1926).

<sup>6</sup> Blix and Wirbelauer, *Ber.*, 36, 4220 (1903); Stähler, *Ber.*, 38, 2629 (1905); Ruff and Eisner, *Ber.*, 41, 2150, 2251 (1908).

formula.<sup>7</sup> The action of the potassium ammonio base on titanium bromide-nitride takes place as represented by the equation,



This potassium salt of an ammonio titanic acid is vigorously hydrolyzed by the action of water to aquo titanic acid, potassium hydroxide and ammonia.

**Ammonio Germanic Acids.** 1. *Germanic Imide*,  $\text{Ge}(\text{NH})_2$ . The germanium analog of cyanamide is obtained as a white, amorphous powder by the action of liquid ammonia on germanic chloride,  $\text{GeCl}_4 + 2\text{NH}_3 = \text{Ge}(\text{NH})_2 + 4\text{HCl}$ .<sup>8</sup>

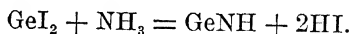
Johnson and Sidwell<sup>9</sup> have recently obtained pure specimens of germanic imide by the ammonolytic action of liquid ammonia on germanic iodide.

2. *Germanam*,  $(\text{Ge})_2\text{NH}$ , which is the germanium analog of dicyanamide,  $(\text{NC})_2\text{NH}$ , and of silicam,  $(\text{NSi})_2\text{NH}$ , was obtained by Schwarz and Schenk by heating germanic imide at  $150^\circ$ . When germanam is heated at  $300^\circ$  germanic nitride is formed.

Attempts have not been made to prepare alkali metal salts of the ammonio germanic acids.

**Ammonio Germanic Acid Esters.** Johnson and Sidwell showed that ethylamine acts on germanic iodide to form the compound represented by the formula,  $\text{Ge}(\text{NC}_2\text{H}_5)_2$ , which is the germanium analog of N-N'-diethylcyanamide. It may be said to be a diethyl ammonogermanate.

**Ammonio Germanous Acids.** *Germanous Imide*,  $\text{GeNH}$ . The ammonio germanous acid, which is the germanium analog of hydrocyanic acid, has been obtained as a yellow, insoluble powder by the ammonolytic action of liquid ammonia on germanous iodide.<sup>10</sup>



The compound readily hydrolyzes to germanous hydroxide and ammonia.

**Ammonio Zirconic Acids.** Stähler and Denk,<sup>11</sup> assumed that zirconium tetramide is formed when the product of the action of liquid ammonia on zirconium iodide is washed with liquid ammonia. Their product however was far from pure.

<sup>7</sup> Ruff and Treidel, *Ber.*, **45**, 1364 (1912); Franklin and Hine, *J. Am. Chem. Soc.*, **34**, 1497 (1912).

<sup>8</sup> Thomas and Pugh, *J. Chem. Soc.*, **1931**, 66; Thomas and Southwood, *J. Chem. Soc.*, **1931**, 2083; Schwarz and Schenk, *Ber.*, **63**, 297 (1930); Fernelius, Thesis Stanford University, 1928.

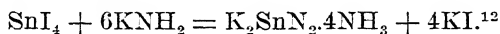
<sup>9</sup> Johnson and Sidwell, *J. Am. Chem. Soc.*, **55**, 1884 (1933).

<sup>10</sup> Johnson, Morey and Kott, *J. Am. Chem. Soc.*, **54**, 4278 (1932).

<sup>11</sup> Stähler and Denk, *Ber.*, **38**, 2517 (1905).

**Ammono Stannic Acids.** Of the theoretically possible ammono stannic acids but one is known and that in the form of its potassium salt only.

*Potassium Ammonostannate*,  $K_2SnN_2 \cdot 4NH_3$ . When potassium amide in excess is added to a liquid ammonia solution of stannic iodide a precipitate of tetrammonated potassium ammonostannate is formed as represented by the equation,



In contrast with the impure, amorphous ammonosilicate and ammonotitanate prepared as described above the ammonostannate was obtained in the form of microcrystals of sharply definite composition.

Potassium ammonostannate may be represented as a tetrammonated salt of stannocyanamide,  $N \equiv Sn-NK_2 \cdot 4NH_3$ , as a triammonated salt of stannoguanidine,  $HN \equiv Sn(NHK)_2 \cdot 3NH_3$ , as a diammonated salt of ortho ammono stannic acid,  $(H_2N)_2Sn(NHK)_2 \cdot 2NH_3$ , as a molecular compound of stannic amide and potassium amide,  $Sn(NH_2)_4 \cdot 2KNH_2$ , or following Werner,<sup>13</sup> and Pauling,<sup>14</sup> as a coordination compound,  $K_2Sn(NH_2)_6$ .

**Ammono Stannous Acid.** *Stannous Imide*,  $Sn-NH$ , is formed as a brown amorphous precipitate when a dilute solution of ammonium bromide in liquid ammonia is added to a similar solution of potassium ammonostannite. The reaction involved is represented by the equation,  $SnNK \cdot 2NH_3 + NH_4Br = SnNH + KBr + 3NH_3$ , or in principle and more simply,  $SnNK + HBr = SnNH + KBr$ .<sup>15</sup> Like stannous hydrous oxide stannous imide is an amphoteric compound. It dissolves in a liquid ammonia solution of ammonium thiocyanate to form stannous thiocyanate and in a solution of potassium amide to yield potassium ammonostannite. When heated in vacuum to 340° stannous imide loses ammonia and passes over into stannous nitride.

*Potassium Ammonostannite*,  $SnNK \cdot 2NH_3$ . According to Bergstrom<sup>16</sup> this compound is formed as represented by the equation,  $10Sn + 6KNH_2 = 2SnNK \cdot 2NH_3 + K_4Sn_6$ , when metallic tin is treated with a liquid ammonia solution of potassium amide. It is interesting to note that the reactions involved are analogous to those which take place when chlorine, or sulfur or phosphorus, for example, is treated with aqueous potassium hydroxide or when sul-

<sup>12</sup> Fitzgerald, *J. Am. Chem. Soc.*, **29**, 1693 (1907).

<sup>13</sup> Werner, "Neuere Anschauung auf dem Gebiete der anorganischen Chemie," Braunschweig, 1913, p. 154.

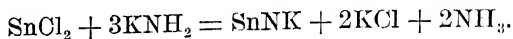
<sup>14</sup> Pauling, *J. Am. Chem. Soc.*, **55**, 1898 (1933).

<sup>15</sup> Bergstrom, *J. Phys. Chem.*, **32**, 438 (1928).

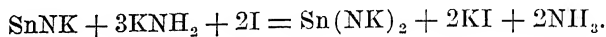
<sup>16</sup> Bergstrom, *J. Phys. Chem.*, **30**, 15 (1926).



fur is dissolved in liquid ammonia. Bergstrom also prepared potassium ammonostannite by the action of potassium amide on stannous chloride,



Just as potassium aquostannite may be oxidized to the aquostannate in water solution so by the action of iodine and an excess of potassium amide in liquid ammonia solution potassium ammonostannite has been nitridized to potassium ammonostannate.<sup>17</sup> The reaction involved may be represented by the equation,



*Sodium Ammonostannite*,  $\text{SnNNa.NH}_3$ . Bergstrom prepared this salt by the action of sodium amide on metallic tin after the manner indicated above for the preparation of the potassium salt. Both potassium ammonostannite and sodium ammonostannite are very soluble in liquid ammonia.

**Thorium Amide**,  $\text{Th}(\text{NH}_2)_4$ , **Thorium Imide**,  $\text{Th}(\text{NH})_2$ . According to Chauvenet<sup>18</sup> thorium amide, thorium imide and thorium nitride are formed successively when the product of the action of liquid ammonia on thorium tetrachloride is heated finally to redness.

<sup>17</sup> Bergstrom, *J. Phys. Chem.*, 32, 449 (1928).

<sup>18</sup> Chauvenet, *Ann. chim. phys.*, [8] 23, 469 (1911).

## CHAPTER XIV.

### HYDRAZOIC ACID.

Some of the methods for the preparation of hydrazoic acid and many of its reactions lead fairly definitely to the conclusion that it is an ammonio nitric acid. Other methods of preparation and a few of the reactions of hydrazoic acid are best explained on the assumption that it is a cyclic nitrous acid hydrazide while certain minor considerations lend some support to the view that it is a cyclic ammonio hyponitrous acid. In this situation, which will be discussed in some detail as we proceed, it seems reasonable to say that hydrazoic acid is a tautomeric compound to which any one of

the formulas,  $\text{HN}=\text{:N}:\text{:N}$ ,  $\begin{smallmatrix} \text{HN}:\text{N} \\ \text{N} \end{smallmatrix}$  or  $\text{HN}=\begin{smallmatrix} \text{:N} \\ \text{:N} \end{smallmatrix}$ , may be ascribed.<sup>1</sup> The

first formula represents the hydrazoic acid molecule as containing two ammonia nitrogen atoms and a nitric acid nitrogen atom, the second, one nitrous acid nitrogen atom and two nitrogen atoms in the state in which they exist in hydrazine. In the third formula two of the nitrogen atoms are hyponitrous acid nitrogen, the third, ammonia nitrogen.<sup>2</sup>

After calling attention to certain striking similarities in the behavior of nitric acid and hydrazoic acid toward reducing agents Turrentine<sup>3</sup> expressed his conception of the nature of hydrazoic acid in the following words.

"Assuming that an analogous reaction implies an analogous structure, the formula,  $\text{H}-\text{N}=\text{N}=\text{N}$ , is proposed for hydronitric acid, which is a parallel formula to  $\text{HONO}_2$ , commonly accepted as representing the structure of nitric acid. In the one instance pentavalent nitrogen, the nucleus of the molecule, is united to nitrogen, and in the

<sup>1</sup> The reader will recall the sense in which it has been proposed to use small plus and minus signs, the colon and double colon.

<sup>2</sup> Browne and Wilcoxson [*J. Am. Chem. Soc.*, **48**, 683 (1926)] say that "hydrazoic acid may therefore be looked upon as *hydrazo nitrous acid*, a nitrous acid of the hydrazine system, experimentally obtainable by *hydrazinolysis* of nitrous acid." This statement implies that hydrazine is to be regarded as the parent substance of a system of compounds in the same way that water and ammonia are taken to be the parent substances respectively of the oxygen and nitrogen systems. It may be noted in this connection that hydrazine is a nitrogen analog of hydrogen peroxide and that as such it belongs to the nitrogen system in the same sense that hydrogen peroxide may be said to belong to the oxygen system. Hydrazino nitrous acid is a reasonable enough name for a nitrous acid hydrazide.

<sup>3</sup> Turrentine, *J. Am. Chem. Soc.*, **34**, 386 (1912).

other, to oxygen. . . . Hydronitric acid, then, must be regarded as a nitridizing agent, analogous to nitric acid, an oxidizing agent, and just as nitric acid is a hydrated oxide of nitrogen, hydronitric acid may come to be regarded as an ammoniated nitride of nitrogen."

Sometime before the publication of Turrentine's paper Thiele<sup>4</sup> attempted to show that the structure of hydrazoic acid is to be represented by the formula,  $\text{H-N-N}\equiv\text{N}$ , rather than by the cyclic formula of Fischer and Curtius. At about the same time the writer<sup>5</sup> speculating upon the possible existence of a nitric acid of the nitrogen system came to look upon hydrazoic acid as an ammono nitric acid and as such to have its constitution represented by the formula  $\text{HN-N}\equiv\text{N}$ , it being understood that the middle nitrogen represents nitric acid nitrogen, the outer two ammonia nitrogen.

*Formation.* 1. On the assumption that hydrazoic acid is an ammono nitric acid it was surmised that it might be possible to obtain the acid by the ammonolysis of aquo nitric acid in accordance with the equation,  $\text{HONO}_2 + 2\text{NH}_3 = \text{HNNN} + 3\text{H}_2\text{O}$ . No reaction took place when either ammonium nitrate or potassium nitrate was heated in liquid ammonia solution. However it was found that hydrazoic acid in the form of its potassium salt, together with potassium hydroxide, is obtained when a liquid ammonia solution containing potassium nitrate and potassium amide is heated for a time at temperatures around  $80^\circ$  to  $90^\circ$ .<sup>6</sup>

It was later found that higher temperatures up to  $120^\circ$  to  $140^\circ$  give better yields in a shorter time. At still higher temperatures  $200^\circ$  or higher, liberal quantities of nitrogen are set free and the yields of potassium azide are lower.<sup>7</sup>

Representing the reaction involved by the equation,



and assuming that the nitric acid nitrogen present in potassium aquonitrate persists as such in potassium azide it will be clear that potassium aquonitrate undergoes ammonolysis to form potassium ammononitrate.

Following the above procedure and using potassium amide in excess yields of potassium azide as high as seventy-five per cent of the amount calculated on the basis of the above equation were obtained. By using sodium nitrate and sodium amide yields of sodium azide

<sup>4</sup> Thiele, *Ber.*, **44**, 2522 (1911).

<sup>5</sup> Franklin, *Eighth Int. Cong. App. Chem.*, **6**, 119 (1912).

<sup>6</sup> Franklin, *Science*, **56**, 28 (1922).

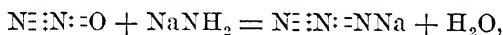
<sup>7</sup> Franklin, *J. Am. Chem. Soc.*, **56**, 568 (1934).

up to sixteen per cent were obtained, while an eighty per cent yield of lead azide was achieved by heating lead nitrate with an excess of potassium amide in liquid ammonia solution. It is interesting to add that attempts to ammonolyze potassium nitrate by heating liquid ammonia solutions of this salt together with potassium amide in a closed steel tube were unsuccessful. Iron was found to inhibit the formation of potassium azide. Chuck<sup>9</sup> identified potassium azide as a product of the action of fused potassium amide on potassium nitrate in an atmosphere of ammonia.

Browne and Wilcoxon<sup>10</sup> obtained good yields of sodium azide by the action of fused sodium amide on sodium nitrate.

The reaction represented by the above equation read from right to left has not been accomplished, that is to say potassium azide has not been converted into aquo potassium aquonitrate by the hydrolytic action of water alone or of a water solution of potassium hydroxide or of sulfuric acid.

2. Assuming that nitrous oxide has the structure represented by the formula,  $\text{N}\equiv\text{N}::\text{O}$ , it follows that the well-known method for the preparation of sodium azide by the action of nitrous oxide on sodium amide in accordance, let us say, with the equation,



may be explained as consisting in the formation of a sodium ammononitrate by the interaction of nitric anhydride-ammonide and the sodium ammono base. The formation of sodium azide takes place when nitrous oxide is passed over hot fused sodium amide<sup>11</sup> or by the action of the gas on sodium amide in liquid ammonia solution.<sup>12</sup> According to Wislicenus zinc azide in small yield is obtained when nitrous oxide is passed over hot zinc amide.

Since however nitrous oxide is formed by the loss of water from aquo hyponitrous acid,  $\begin{array}{ccc} \text{N}::\text{OH} & & \text{N} \\ \vdots & & \vdots \\ \text{N}::\text{OH} & \xrightarrow{-\text{H}_2\text{O}} & \text{N}::\text{O} \end{array}$ , one might reasonably say

that it is an hyponitrous anhydride which reacts with sodium amide to form a cyclic sodium ammonohyponitrite. Browne and Wilcoxon<sup>13</sup> have suggested that hydrazoic acid may be regarded as an ammono hyponitrous acid.

3. Hydrazoic acid, nitrous oxide, nitrogen, water and ammonia are formed by the interaction of hydrazine and nitrous acid in water

<sup>9</sup> Faw Yap Chuck, Thesis, Stanford University, 1925.

<sup>10</sup> Browne and Wilcoxon, *J. Am. Chem. Soc.*, **48**, 682 (1926).

<sup>11</sup> W. Wislicenus, *Ber.*, **25**, 2084 (1892); Dennis and Browne, *J. Am. Chem. Soc.*, **26**, 577 (1904).

<sup>12</sup> Joannis, *Compt. rend.*, **118**, 714 (1894).

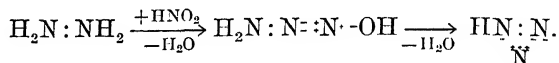
<sup>13</sup> Browne and Wilcoxon, *J. Am. Chem. Soc.*, **48**, 685 (1926).

solution, the relative yields depending upon conditions which need not be considered here.<sup>14</sup>

Angeli<sup>15</sup> obtained silver azide by bringing silver nitrite and hydrazine sulfate together in water solution.

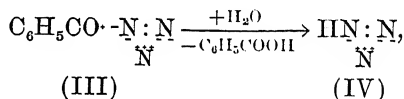
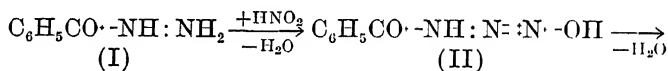
Dennstedt and Göhlich<sup>16</sup> prepared hydrazoic acid by the interaction of potassium nitrite and hydrazine sulfate in aqueous sulfuric acid.

The most obvious explanation of the appearance of hydrazoic acid among the products of the interaction of hydrazine and nitrous acid is to the effect that a cyclic nitrous acid hydrazide is formed in accordance with the equation,



The action of hydrazine and its derivatives on nitrous acid and the diazo compounds will be discussed in some detail later.

4. Curtius first obtained hydrazoic acid by hydrolyzing benzoic azide which is formed by the action of nitrous acid on benzoic hydrazide.<sup>17</sup> The reactions concerned may be represented by the scheme,



and interpreted as consisting in the successive formation of two benzoic acid nitrous acid hydrazides, (II) and (III), followed by the hydrolysis of benzyoyl azide, (III), to aquo benzoic acid and the cyclic nitrous acid hydrazide (IV).

5. Hydrazoic acid is among the products of the action of certain oxidizing agents on hydrazine.<sup>18</sup> Supplementing the speculation of the authors referred to above it may be assumed that the formation of hydrazoic acid by the action of oxidizing agents on hydrazine takes place in accordance with the equations,

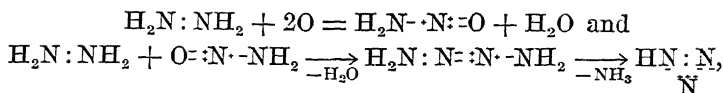
<sup>14</sup> Curtius, *Ber.*, **26**, 1263 (1893); Sommer and Pincas, *Ber.*, **49**, 259 (1916).

<sup>15</sup> Angeli, *Atti. accad. lincei*, [5] **2**, I, 568 (1893).

<sup>16</sup> Dennstedt and Göhlich, *Chem. Ztg.*, **21**, 876 (1897).

<sup>17</sup> Curtius, *Ber.*, **23**, 3028 (1900).

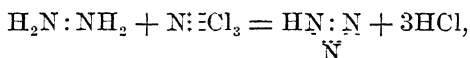
<sup>18</sup> Bray and collaborators, *J. Am. Chem. Soc.*, **46**, 858, 1788, 1796, 1810 (1924); Browne, *J. Am. Chem. Soc.*, **27**, 551 (1905); Browne and Sletterly, *J. Am. Chem. Soc.*, **29**, 1305 (1907); **30**, 53 (1908); **31**, 221, 783 (1909).



the first of which represents the oxidation of hydrazine to an unknown aquo-ammono nitrous acid which should decompose directly to form nitrogen (nitrous anammonide) and ammonia or react with a second molecule of hydrazine as represented by the second equation to form a nitrous acid hydrazide and water. This open chain hydrazide, which is known in the form of derivatives, losing ammonia passes over into the cyclic nitrous acid hydrazide, namely hydrazoic acid. The formation of phenylazide by the action of augmenting agents on certain diazo compounds is discussed in Chapter XXXI.

5. Good yields of hydrazoic acid have been obtained by shaking a benzene solution of nitrogen trichloride with a water solution of hydrazine.<sup>19</sup>

Since the mechanism of the reactions concerned is not obvious it is perhaps best to say simply that hydrazine, under the action of hypochlorous acid chlorine, is nitridized to ammono nitric acid. However it is interesting to observe that the formation of hydrazoic acid as thus accomplished may be explained on the assumption that a hypothetical nitrous acid chloride, which would be a tautomer or at any rate a potential form of hypochlorous anammonide, acts on hydrazine as represented by the equation,



to form a nitrous acid hydrazide. In view of the fact that the negativity of chlorine is only slightly less than that of nitrogen<sup>20</sup> it is perhaps fair to assume that, depending upon conditions, nitrogen trichloride is ready to act either as a chlorine nitride or as a nitrous acid chloride.

*Structure.* It will be clear from the above discussion that in so far as methods of preparation are concerned no definite conclusions can be drawn in respect to the constitution of hydrazoic acid. In the liquid state and in the form of its alkyl and aryl derivatives it is probably best looked upon as a tautomeric mixture of the open chain and cyclic forms in which the latter perhaps predominates since determinations of the parachors of a number of liquid azides<sup>21</sup> are in harmony with the cyclic structure of the azide group. On

<sup>19</sup> Tanatar, *Ber.*, 32, 1399 (1899).

<sup>20</sup> Pauling, *J. Am. Chem. Soc.*, 54, 3677 (1932).

<sup>21</sup> Lindemann and Thiele, *Ber.*, 61, 1529 (1928); Götzky, *Ber.*, 64, 1557 (1931).

the other hand crystal structure measurements show that salts hydrazoic acid are to be represented by the chain formula.<sup>22</sup>

We shall find as we proceed that the reactions into which hydrazoic acid enters do not definitely establish its structure. The large majority of its reactions are reasonably explained on the assumption that it is an ammonio nitric acid, others equally readily on the assumption that it is either an ammonio nitric acid or a nitro acid hydrazide while a few seem to require that it act as a nitro acid hydrazide. None apparently demands that hydrazoic acid act as an ammonio hyponitrous acid.

**Hydrazoic Acid as a Nitridizing Agent.** Looking upon hydrazoic acid as the ammonia analog of ordinary nitric acid then just as the latter acid is familiarly known to be a powerful oxidizing agent so one might expect hydrazoic acid to exhibit in a more or less conspicuous manner the properties of a nitridizing agent. As a matter of fact many of the reactions into which hydrazoic acid enters show that it possesses such properties.

**Action on Metals.** In liquid ammonia solution hydrazoic acid acts on sodium, potassium, lithium, calcium and magnesium with the formation of the respective metallic azides and hydrogen gas. In these reactions no augmentation is involved beyond the deelectronation of the metals to their respective ions and the reduction of ionic hydrogen to elementary hydrogen. The azide group remains intact.

In water solution on the other hand hydrazoic acid attacks certain metals to form metallic azides, nitrogen and ammonia, and not with the evolution of hydrogen as originally reported by Curtius and Rissom,<sup>24</sup> in their account of the action of hydrazoic acid on metals.

Some years ago Turrentine and Moore<sup>25</sup> observed that in aqueous solution hydrazoic acid acts on metallic copper to form cupric azide, nitrogen and ammonia. More recently it has been shown in this laboratory<sup>26</sup> that aqueous hydrazoic acid acts on zinc, iron, manganese, nickel and copper without the evolution of hydrogen with the respective metallic azides, nitrogen and ammonia together with small amounts of hydrazine, and that metallic magnesium dissolves with the formation of magnesium azide, nitrogen, ammonia, hydrazine

<sup>22</sup> Hendricks and Pauling, *J. Am. Chem. Soc.*, **47**, 2904 (1925); Günther, Porger and Rosbaud, *Z. physik. Chem.*, **6**, B, 459 (1930).

<sup>23</sup> Browne and Houlehan, *J. Am. Chem. Soc.*, **33**, 1750 (1911).

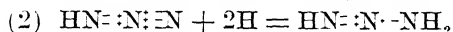
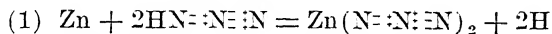
<sup>24</sup> Curtius and Rissom, *J. prakt. Chem.*, [2] **58**, 267, 291, 298 (1898); Curtius and Darapsky, *J. prakt. Chem.*, [2] **61**, 420 (1900).

<sup>25</sup> Turrentine and Moore, *J. Am. Chem. Soc.*, **34**, 382 (1912).

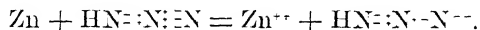
<sup>26</sup> Faw Yap Chuek, Thesis, Stanford University, 1925; J. B. Harker, Thesis, Stanford University, 1927; E. E. Goodyear, Thesis, Stanford University, 1928; Franklin, *J. Am. Chem. Soc.*, **56**, 568 (1934).

zinc and hydrogen. It will be recalled that hydrogen is among the products of the action of nitric acid on magnesium. Cooke<sup>26a</sup> identified hydrazine among the products of the action of reducing agents on hydrazoic acid.

The action of aqueous hydrazoic acid on zinc, iron, manganese, nickel and copper resembles in a very striking way the action of ordinary nitric acid on the same metals. When, for example, metallic zinc dissolves in aquo nitric acid zinc nitrate and, depending upon conditions, various reduction products of nitric acid are formed. Nitric acid oxidizes the zinc while simultaneously zinc reduces the nitric acid. Similarly under the action of hydrazoic acid metallic zinc is nitridized (augmented) to the dipositive state while at the same time the ammono nitric acid is reduced, let us say, to ammono nitrous acid. This unknown compound immediately loses ammonia to form an hypothetical nitrous anammonide which of course appears as elementary nitrogen. The reactions involved may be represented by the equations,



It is of course not necessary to say that hydrogen ions are first reduced by the zinc and that the nascent hydrogen thus formed in turn reduces the ammono nitric acid to the hypothetical ammono nitrous acid. Much more reasonably it may be assumed that the zinc reduces the nitric acid directly as represented, in principle, by the equation,



Two electrons passing from the zinc atom to the nitric acid nitrogen atom brings about the augmentation of zero valent zinc to the zinc ion and the reduction of nitric acid nitrogen to nitrous acid nitrogen. In any event, and independently of what the mechanism of the reactions involved may be, it is clear that the action of hydrazoic acid on metallic zinc closely resembles that of aquo nitric acid on the same metal.

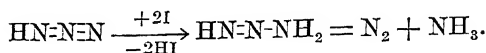
**Action on the Halogen Acids.** 1. Hydrazoic acid, in water solution, nitridizes hydriodic acid forming iodine, nitrogen and ammonia.<sup>26b</sup> As has already been done in explanation of the action of zinc on hydrazoic acid it is reasonable to suppose that an ammono

<sup>26a</sup> Cooke, *Proc. Chem. Soc.*, **19**, 213 (1903).

<sup>26b</sup> Hofmann, Hock and Kirmreuther, *Ann. Chem.*, **380**, 140 (1911); Browne and Hoel, *J. Am. Chem. Soc.*, **44**, 2116 (1922).



nitrous acid is the primary product of the reducing action of hydriodic acid on ammonio nitric acid,



2. Browne and Hoel have also shown that small amounts of chlorine are set free when a water solution containing hydrochloric acid and hydrazoic acid is heated to boiling, while observations made in this laboratory have shown that bromine is formed when sodium azide is heated with aqueous hydrobromic acid.

3. A mixture of hydrochloric acid and hydrazoic acid in water solution shows the properties of aqua regia to the extent at least that such a mixture dissolves gold and platinum.<sup>27</sup>

A water solution containing sodium azide and hydrochloric acid, together with a few centigrams of metallic gold, was sealed in a glass tube and heated in a water bath to 100°. After a few minutes it was obvious from the yellow color of the liquid that the gold was going into solution. After an hour the gold had disappeared and the solution had taken on the strong yellow color of a solution of auric chloride. Addition of stannous chloride to a small portion of the solution, diluted for the purpose of the test, gave the purple of Cassius reaction. Furthermore, metallic gold was recovered from the solution by the reducing action of ferrous sulfate.

A few centigrams of platinum black was similarly heated in a sealed tube with an aqueous solution of sodium azide and hydrochloric acid. The platinum was attacked and after a time a precipitate of ammonium chlorplatinate appeared, the ammonia required for the formation of this salt resulting from the reduction of hydrazoic acid. Neither gold nor platinum is attacked when heated with liquid ammonia solutions of ammonium azide and ammonium chloride at temperatures as high as 200°.<sup>27a</sup>

Presumably the reactions here involved run more or less closely parallel to those which take place when aqua regia dissolves platinum. It is known that aqua regia augments hydrochloric acid to chlorine and is itself reduced to a nitrous acid chloride,

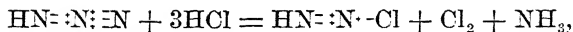


The purely hypothetical equation,

<sup>27</sup> Turrentine, *J. Am. Chem. Soc.*, **34**, 385 (1912); Franklin, *J. Am. Chem. Soc.*, **56**, 568 (1934); Curtius and Risom [*J. prakt. Chem.*, [2] **58**, 268 (1898)] retract an earlier somewhat tentative statement by Curtius [*Ber.*, **23**, 3027 (1890)] to the effect that the noble metals are attacked by aqueous hydrazoic acid.

<sup>27a</sup> Unpublished observations.

<sup>28</sup> Goldschmidt, *Ann. Chem.*, **205**, 372 (1880); Lunge and Pelet, *Z. ang. Chem.*, **8**, 3 (1895).

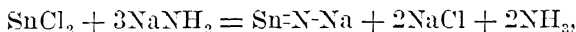


may be written to represent the interaction of hydrazoic acid and hydrochloric acid. The nitrous acid imide-chloride breaks down to form nitrogen (nitrous anammonide) and hydrochloric acid. The nascent chlorine augments metallic platinum to form platinum chloride which unites with the ammonium chloride formed in the solution to give ammonium chloroplatinate.

*Action on Certain Inorganic Compounds.* 1. When sodium azide is added to a solution of ferrous sulfate, made acid by the addition of hydrochloric acid, and the solution is warmed, the ferrous iron is augmented to ferric iron. So also according to Harker ferrous azide formed by dissolving metallic iron in aqueous hydrazoic acid, is augmented to the ferric salt when the solution is warmed with an excess of the acid.

2. Hydrazoic acid augments hydrogen sulfide in water solution to elementary sulfur<sup>29</sup> and finally to sulfuric acid.

3. Chuck dissolved stannous chloride in molten sodium amide in an atmosphere of ammonia. Presumably a mixture of sodium ammonostannite and sodium chloride in solution in fused sodium amide was formed. It was found on dissolving the melt in water that the tin was present as stannous tin. In a second experiment sodium azide was gradually added to the yellow melt, formed by dissolving stannous chloride in fused sodium amide, until the color had disappeared. The cold cake was treated first with water and then with hydrochloric acid. The tin in the solution thus formed was found to be in the stannic state. It follows from these observations that a sodium ammonostannite, formed by dissolving stannous chloride in an excess of molten sodium amide,



is nitridized to a sodium ammonostannate by the action of sodium ammononitrate,  $\text{Sn}=\text{N}-\text{Na} + \text{NaN}=\text{N}=\text{N} = \text{Na}=\text{N}-\text{Sn}=\text{N}-\text{Na} + \text{N}_2$ . It will be recalled that potassium and sodium ammonostannites and ammonostannates have been prepared. (*Cf.* Chapter XIII.)

4. According to Raschig<sup>30</sup> stannous chloride in hydrochloric acid solution reduces hydrazoic acid to ammonia and nitrogen which in other words is to say that hydrazoic acid augments stannous chloride to stannic chloride,



<sup>29</sup> Hart, *J. Am. Chem. Soc.*, **50**, 1924 (1928).

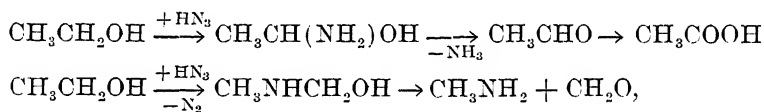
<sup>30</sup> Raschig, "Schwefel- und Stickstoffstudien," p. 213, Leipzig-Berlin.

It is reasonable to suppose that an ephemeral ammonio nitrous acid is formed which immediately decomposes to form nitrogen and ammonia.

5. The addition of sodium azide to fused sodium cyanide converts the latter into disodium cyanamide. As has already been shown (*cf.* Chapter XII, p. 130) the reaction involved consists in the nitridation of sodium ammonocarbonite to a sodium ammonocarbonate.

*Action on Alcohols, Aldehydes and Ketones.* Just as nitric acid energetically oxidizes the alcohols, aldehydes and ketones so one might expect to find these compounds ready to undergo nitridation, or in general terms augmentation, under the action of hydrazoic acid. Of the limited number of reactions of this kind which have been studied the following are examples.

1. Chuck <sup>31</sup> found that acetaldehyde, acetic acid, methylamine and ammonia are formed when a water solution containing ethyl alcohol, sodium azide and sulfuric acid is heated. A reasonable explanation of Chuck's results is embodied in the schemes,



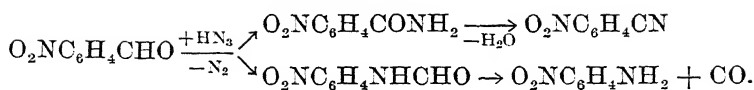
in accordance with which ethyl alcohol is augmented partly to aldehyde ammonia and partly to the formaldehyde acetal,  $\text{CH}_3\text{N}(\text{H})\text{CH}_2\text{OH}$ . The former compound in the presence of sulfuric acid yields acetaldehyde which in turn is augmented to acetamide. This aquo-ammonio acetic acid is then hydrolyzed to aquo acetic acid and ammonia. The latter compound, in acid solution, breaks down to form aquo formaldehyde and methylamine. Chuck was unable to identify formaldehyde or formic acid among the reaction products. He did not test for carbon dioxide.

2. Benzyl alcohol heated in a similar manner with sodium azide and dilute sulfuric acid was found by Chuck to yield benzaldehyde, benzoic acid and aniline in fair quantities though the chief product formed was a tarry oil the nature of which remains unknown.

3. According to Schmidt <sup>32</sup> *m*-nitrophenylcyanide, *m*-nitraniline and carbon monoxide are formed when a mixture containing hydrazoic acid, benzene, sulfuric acid and *m*-nitrobenzaldehyde is gently heated. The reactions involved may be explained as taking place as represented by the scheme,

<sup>31</sup> Faw Yap Chuck, Thesis, Stanford University, 1925.

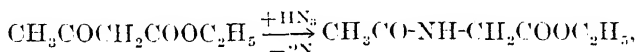
<sup>32</sup> Schmidt, *Ber.*, 57, 704 (1924); *Chem. Abstracts*, 19, 3248 (1925).



In accordance with the upper branch of the scheme the aquo aldehyde is nitridized to a carboxazylic acid (an acid amide) which in the presence of strong sulfuric acid is dehydrated to the corresponding acid anammonide. In accordance with the lower branch the aldehyde is nitridized to a carboxazylic acid ester. This N-ester of an aquo-ammono formic acid breaks down under the action of sulfuric acid to form *m*-nitraniline and carbon monoxide after the manner of the decomposition of formamide to ammonia and carbon monoxide.

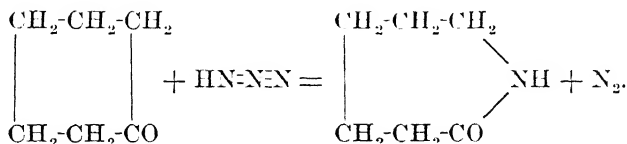
4. Under similar treatment acetone is converted practically quantitatively into methylacetamide, which is to say that an aquo ketone is nitridized by the action of ammono nitric acid to the N-methyl ester of aquo-ammono acetic acid as represented by the equation,  $(\text{CH}_3)_2\text{CO} + \text{HN}=\text{N}=\text{N} = \text{CH}_3\text{CONHCH}_3 + \text{N}_2$ . The reaction involved is strictly analogous to that of the action of oxidizing agents on acetone. In the one case the ester of a carboxazylic acid is obtained in the other, since methyl aquo acetate is readily hydrolyzed, the free carboxylic acid, namely aquo acetic acid, results. By the same treatment benzophenone has been converted quantitatively into benzanilide.

5. Schmidt has shown furthermore that acetoacetic ester reacts with hydrazoic acid as represented by the equation,



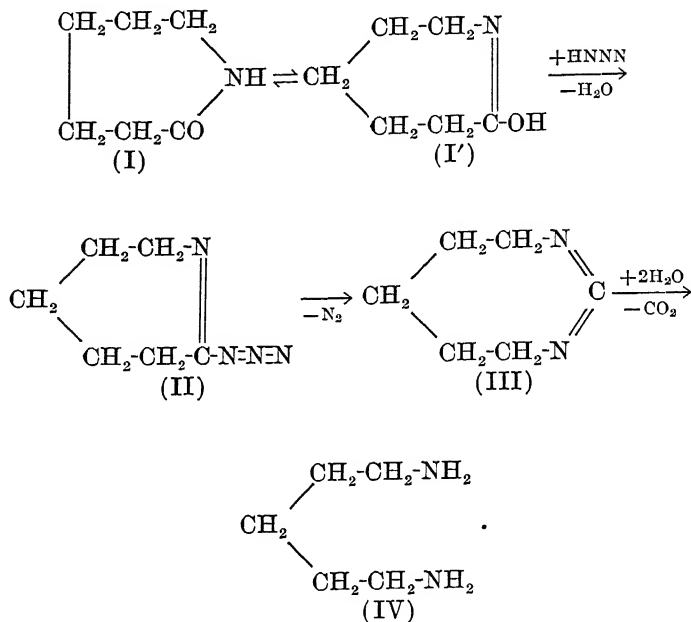
to form ethyl acetylaminooacetate. A ketone is thereby nitridized to a derivative of a carboxazylic acid.

6. So also are cyclic ketones nitridized by the action of hydrazoic acid, cyclohexanone for example, to form a cyclic carboxazylic acid ester known as  $\epsilon$ -leucinelactam,



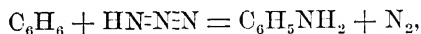
7. When cyclohexanone is treated with hydrazoic acid in excess under the conditions described by Schmidt an azide, formula (II) below, of the cyclic carboxazylic acid ester (I) (I') is formed which,

when heated with hydrochloric acid in a closed tube, is converted into pentamethylenediamine, carbon dioxide and nitrogen in a manner which may be represented as follows,



The successive reactions involved may be said to consist first, in the conversion of a cyclic carboxazylic acid ester (I) (I') into a cyclic carbazylic acid ester azide (II), second, in the intramolecular nitridation and reduction of this compound to form a cyclic ammono carbonic acid ester, (III), and nitrogen, in principle a Curtius rearrangement, and third, in the hydrolysis of this cyclic ester (III) to the diatomic ammono alcohol, (IV), and carbon dioxide.

S. Schmidt reports that a high yield of aniline, together with small amounts of hydrazine and hydroxylamine, is obtained when a benzene solution of hydrazoic acid is shaken with concentrated sulfuric acid at 60°. The formation of aniline may be represented by the equation,

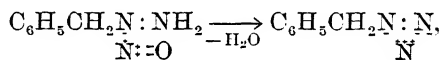


and explained as consisting in the nitridation of benzene to an ammono phenol or in general terms of a hydrocarbon to an ammono alcohol.

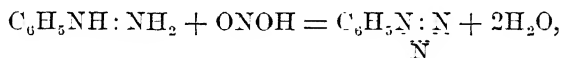
In the above discussion of hydrazoic acid as a nitridizing agent

we have sought to explain its action on the assumption that it is an ammono nitric acid. It may be, however, that a nitrous acid hydrazide or even an ammono hyponitrous acid acts as a nitridizing agent in a manner not distinguishable from that of an ammono nitric acid.

**Alkyl and Aryl Azides.** Apparently but four aliphatic azides, methylazide, ethylazide, ethylenediazide and benzylazide are known. They have been prepared by methods which are in harmony with the view that they are esters of an ammono nitric acid, the first two, by the action of methyl sulfate and ethyl sulfate respectively on sodium azide, the third, by the action of ethylene chloride on sodium azide and the fourth, by the interaction of benzyl iodide and silver azide. However, excepting that under the action of alcoholic alkali hydrazoic acid is very slowly eliminated from ethylenediazide without the liberation of nitrogen gas, these azides resist the action of hydrolyzing agents. It follows that they can hardly be regarded as esters. On the other hand, deducing the structure of benzylazide and of phenylazide on the basis of the preparation of the one by the dehydration of N-nitrosobenzylhydrazine, which is a nitrous acid benzylhydrazide,



and of the other, to take one example out of many available, by the interaction of phenylhydrazine and nitrous acid,



one would conclude that benzylazide is a benzylhydrazide of nitrous acid and that phenylazide is a nitrous acid phenylhydrazide. Moreover the very considerable number of reactions into which phenylazide has been observed to enter are more readily explained on the assumption that it is a phenylhydrazide of nitrous acid rather than a phenyl ammononitrate.

Two important papers, in which the constitution of hydrazoic acid is discussed, have appeared since this chapter was written.<sup>33</sup>

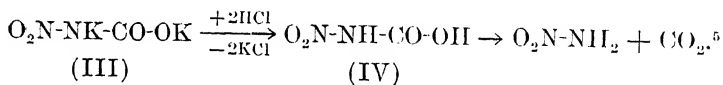
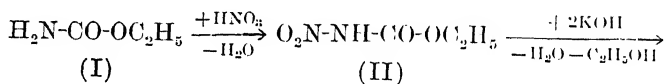
<sup>33</sup> Sidgwick, Sutton and Thomas, *J. Chem. Soc.*, 1933, 406; Hantzsch, *Ber.*, 66, 1349 (1933).

## CHAPTER XV.

### AQUO-AMMONO NITRIC ACID.

**Nitramide.** To this compound the formula,  $\text{H}_2\text{N}\cdot\text{NO}_2$ , was ascribed by its discoverers.<sup>1</sup> Hantzsch,<sup>2</sup> who for a time maintained that Thiele and Lachman's compound is a stereoisomer of hyponitrous acid, came later to the conclusion that it is to be represented by the formula,  $\text{HN}\cdot\text{NO}\cdot\text{OH}$ . Hunter and Partington,<sup>3</sup> as a result of parachor and dipole moment measurement, apparently came to no definite conclusion concerning the constitution of the compound. Here we express the opinion that nitramide is a tautomeric aquo-ammono nitric acid to which any one of the formulas,  $\text{H}_2\text{N}\cdot\text{N}\overset{\overset{\text{O}}{\parallel}}{\text{O}}$ ,  $\text{HN}\cdot\text{N}\overset{\overset{\text{O}}{\parallel}}{\text{OH}}$  or  $\text{N}\overset{\overset{\text{O}}{\parallel}}{\text{N}}\cdot\overset{\overset{\text{O}}{\parallel}}{\text{OH}}$ , may be given.

Thiele and Lachman prepared nitramide from urethane by a succession of reactions which may be summarized by means of the scheme,



Urethane (I), an O-ethyl ester of an aquo-ammono carbonic acid, under the action of nitric acid is converted into nitrourethane (II). When this ethyl ester of a mixed aquo-ammono carbonic aquo-ammono nitric acid is treated with potassium hydroxide it is converted into the dipotassium salt (III). The free acid (IV), formed by the action of hydrochloric acid on this salt, decomposes spontaneously to form nitramide and carbon dioxide.

The properties of nitramide are in entire harmony with the view that it is an aquo-ammono nitric acid. Its water solution reddens

<sup>1</sup> Thiele and Lachman, *Ann. Chem.*, **288**, 267 (1893).

<sup>2</sup> Hantzsch, *Ann. Chem.*, **292**, 352 (1896); *Ber.*, **63**, 1272 (1930).

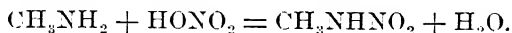
<sup>3</sup> Hunter and Partington, *J. Chem. Soc.*, **1933**, 309.

<sup>5</sup> The potassium atoms in the dipotassium salt of nitrourethane are not necessarily combined as indicated.

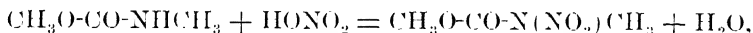
litmus. In solution in water<sup>6</sup> as well as in liquid ammonia<sup>7</sup> it is a fair conductor of electricity. Excepting that a very unstable ammonium salt and a mercuric salt are known attempts to prepare metallic salts have been frustrated by the ease with which these salts undergo decomposition. However the existence of the dipotassium salt of nitrocarbanic acid, formula (III) above, of metallic salts of methylnitramide (p. 156), of nitroguanidine (p. 185), of nitrourea (p. 184), and of arylsulfonylnitramides (p. 186) shows that many derivatives of nitramide are acids of marked strength. Finally the decomposition of nitramide to form nitrous oxide and water,  $\text{H}_2\text{N}-\text{NO}_2 = \text{N}\equiv\text{N}::\text{O} + \text{H}_2\text{O}$ , is reasonably interpreted as consisting in the dehydration of an aquo-ammono nitric acid to form nitric anhydride anammonide. Nitramide has not been hydrolyzed to aquonitric acid and ammonia.

**Esters.** Examples of compounds which are to be regarded as esters of aquo-ammono nitric acid are methylnitramide, dimethylnitramide and dimethylisonitramide represented by the respective formulas,  $\text{CH}_3\text{NH}-\text{NO}_2$ ,  $(\text{CH}_3)_2\text{N}-\text{NO}_2$  and  $\text{CH}_3\text{N}=\text{NO}-\text{OCH}_3$ .

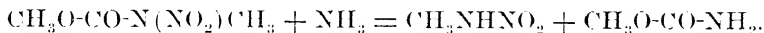
*Methylnitramide*,  $\text{CH}_3\text{NHNO}_2 \rightleftharpoons \text{CH}_3\text{N}=\text{NO}-\text{OH}$ . Looked upon as an N-methyl aquo-ammono nitrate it might be expected that methylnitramide would be formed by the action of nitric acid on methylamine in accordance with the equation,



While methylnitramide has not been so prepared it does happen that a reaction identical in principle takes place as represented by the equation,



when O-N-dimethyl carbamate is treated with concentrated nitric acid. A dimethyl ester of a carbonic nitric acid is formed, which, on treatment in ether solution with ammonia, undergoes ammonolysis to methylnitramide and O-methyl carbamate,



These ammonolytic products are respectively an N-methyl aquo-ammono-nitrate and an O-methyl aquo-ammono-carbonate.<sup>8</sup>

Methylnitramide has also been prepared from methylurea in a manner summarized by the scheme.<sup>9</sup>

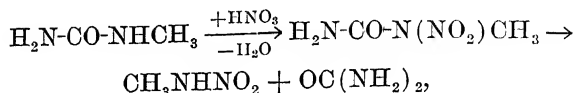
<sup>6</sup> Bauer, *Ann. Chem.*, **296**, 95 (1897).

<sup>7</sup> Franklin and Kraus, *J. Am. Chem. Soc.*, **27**, 208 (1905).

<sup>8</sup> Franchimont and Klobbie, *Rec. trav. chim.*, **7**, 354 (1888).

<sup>9</sup> Degner and v. Pechmann, *Ber.*, **30**, 652 (1897); Backer, *Rec. trav. chim.*, **34**, 187 (1915).

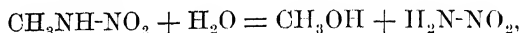




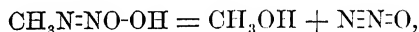
excepting that urea was not identified as one of the products of the reaction.

Methylnitramide when gently warmed with concentrated sulfuric acid gives an abundant yield of nitrous oxide together with a small amount of nitric acid.<sup>10</sup> When warmed with sixty per cent sulfuric acid practically quantitative yields of methyl alcohol and nitrous oxide are obtained.<sup>11</sup> It is reasonable to suppose that the nitric acid is formed by the hydrolysis of the ester in accordance with the equation,  $\text{CH}_3\text{NH-NO}_2 + \text{H}_2\text{O} = \text{CH}_3\text{NH}_2 + \text{HONO}_2$ .

Whether the formation of nitrous oxide and methyl alcohol results from the hydrolysis of methylnitramide,



followed by the decomposition of the nitramide thus formed into nitrous oxide and water or whether the ester decomposes directly, say in accordance with the equation,



is an open question.

Represented by either of the formulas,  $\text{CH}_3\text{NH-NO}_2$  or  $\text{CH}_3\text{N-NO-OH}$ , methylnitramide is an acid ester. Accordingly its water solution shows an acid reaction and is a fair conductor of electricity,<sup>12</sup> while in liquid ammonia solution it is an excellent conductor.<sup>13</sup>

The following metallic salts of methylnitramide have been prepared all of which are stable in the presence of water.  $\text{CH}_3\text{NKNO}_2$  or  $\text{CH}_3\text{N-NOOK}$ ,  $\text{CH}_3\text{O}_2\text{N}_2\text{Na}$ ,  $(\text{CH}_3\text{O}_2\text{N}_2)_2\text{Cu}$ ,  $\text{CH}_3\text{O}_2\text{N}_2\text{Ag}$ ,  $(\text{CH}_3\text{O}_2\text{N}_2)_2\text{Ba.H}_2\text{O}$ ,  $(\text{CH}_3\text{O}_2\text{N}_2)_2\text{Zn}$ ,  $(\text{CH}_3\text{O}_2\text{N}_2)_2\text{Cd}$ ,  $(\text{CH}_3\text{O}_2\text{N}_2)_2\text{Hg}$ ,  $(\text{CH}_3\text{O}_2\text{N}_2)_2\text{Co}$  and  $(\text{CH}_3\text{O}_2\text{N}_2)_2\text{Ni.6H}_2\text{O}$ .

*N-N-Dimethylnitramide*,  $(\text{CH}_3)_2\text{N-NO}_2$ . Four methods for the preparation of this neutral ester of aquo-ammonio nitric acid are the following. It is formed (1) by heating methylnitramide with methyl iodide and alcoholic potassium hydroxide, (2) by the action of diazomethane on nitramide, (3) by dissolving dimethylammonium nitrate in acetic anhydride and (4) by the action of concentrated

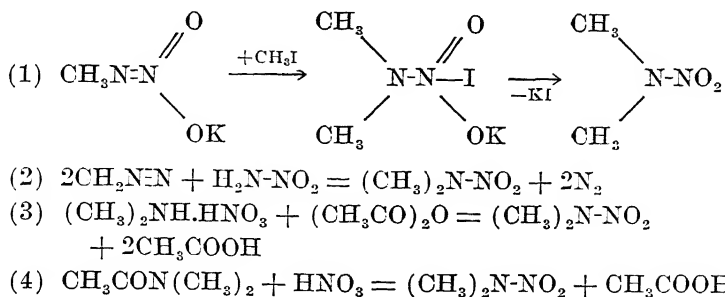
<sup>10</sup> Thiele and Lachman, *Ann. Chem.*, **288**, 269 (1895).

<sup>11</sup> Franchimont and Umbgrove, *Rcc. trav. chim.*, **17**, 288 (1898).

<sup>12</sup> Hantzsch, *Ber.*, **32**, 3066 (1899), 1075 (1904).

<sup>13</sup> Franklin and Kraus, *J. Am. Chem. Soc.*, **27**, 196 (1905).

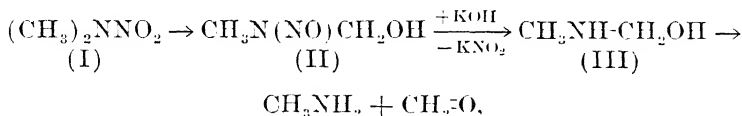
nitric acid on N-N-dimethylacetamide as represented by the respective equations,<sup>14</sup>



The first equation represents the formation of an ester by the familiar action of an alkyl halide on a metallic salt, the second is an example of the well-known methylating action of diazomethane, the third represents the formation of a nitric acid ester by the action of nitric acid on an ammono methyl alcohol. The fourth equation represents the formation of an aquo-ammono nitric acid ester by the action of aquo nitric acid on an N-N-dialkyl ester of an aquo-ammono acetic acid.

The successful reduction of N-N-dimethylnitramide to unsymmetrical dimethylhydrazine<sup>15</sup> supports the view that it is an ester of an aquo-ammono nitric acid in that a derivative of this acid undergoes reduction to a derivative of hydrazine.

Van Erp<sup>17</sup> has shown that methylamine, formaldehyde and potassium nitrite are formed when a mixture of dimethylnitramide (1 gram), potassium hydroxide (4 grams) and water (5 drops) is heated at 180° to 200°. As represented by the equation,



van Erp's results may be explained on the reasonable assumption that by a process of intramolecular oxidation and reduction dimethyl aquo-ammono-nitrate (I) rearranges to a methyl nitrous acid formaldehyde acetal (II), which under the action of potassium

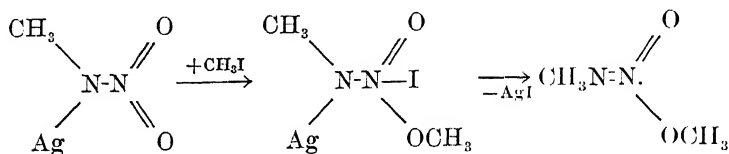
<sup>14</sup> Franchimont, *Rec. trav. chim.*, **2**, 343 (1883); Franchimont and Klobbie, *Rec. trav. chim.*, **7**, 355 (1888); Bamberger, *Ber.*, **28**, 402 (1895); Kirpal, *Ber.*, **28**, 537 (1895); Henke, *Ber.*, **31**, 1395 (1898).

<sup>15</sup> Franchimont, *Rec. trav. chim.*, **3**, 427 (1884); Backer, *Rec. trav. chim.*, **31**, 150 (1912).

<sup>17</sup> Van Erp, *Ber.*, **29**, 474 (1896).

hydroxide is hydrolyzed to methylamine, formaldehyde and potassium nitrite. The transformation of (I) into (II) involves a Beckmann-like rearrangement, in principle the augmentation of an alcohol to an aldehyde and the simultaneous reduction of nitric acid to nitrous acid.

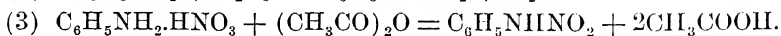
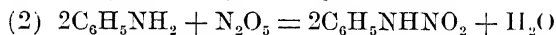
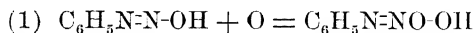
*O-N-Dimethylnitramide*,  $\text{CH}_3\text{N}=\text{NO}-\text{OCH}_3$ . This O-N-dimethyl ester of an aquo-ammono nitric acid has been obtained, along with the N-N-ester, by the action of methyl iodide on the silver salt of methylnitramide,<sup>18</sup> the reactions involved probably taking place as follows,



The intermediate compound has not been isolated.

*Isoamylnitramide*,  $\text{C}_5\text{H}_{11}\text{NH}-\text{NO}_2$ , is formed by the interaction of isoamylchloramine and silver nitrite<sup>19</sup> as represented by the equation,  $\text{C}_5\text{H}_{11}\text{NH}\cdot\text{Cl} + \text{AgNO}_2 = \text{C}_5\text{H}_{11}\text{NH}-\text{NO}_2 + \text{AgCl}$ . This reaction involves the augmentation of the nitrite group and the reduction of the positive chlorine atom. That is to say the hypochlorous acid chlorine contained in amyl ammono hypochlorite augments the nitrous acid nitrogen to nitric acid nitrogen, the hypochlorous acid chlorine simultaneously undergoing reduction to the chlorine ion. A silver salt of this acid ester,  $\text{C}_5\text{H}_{11}\text{N}(\text{Ag})\text{NO}_2$ , is known.

*Phenylnitramide*,  $\text{C}_6\text{H}_5\text{NH}-\text{NO}_2$ . Among the methods by which this N-phenyl ester of an aquo-ammono nitric acid has been obtained are the following,<sup>20</sup> (1) by the action of oxidizing agents on diazobenzene whereby an N-phenyl aquo-ammono nitrite is oxidized to an N-phenyl aquo-ammono nitrate, (2) by adding nitrogen pentoxide to a cold ether solution of aniline and (3) by the dehydrating action of acetic anhydride on aniline nitrate. The reactions involved are represented by the respective equations,



<sup>18</sup> Franchimont and Umbgrove, *Rec. trav. chim.*, 15, 211 (1896).

<sup>19</sup> Berg, *Ann. Chim.*, [7] 3, 357 (1894).

<sup>20</sup> Bamberger and Storch, *Ber.*, 26, 277 (1893); Bamberger and Landsteiner, *Ber.*, 26, 485 (1893); Bamberger, *Ber.*, 27, 363, 584, 1274 (1894); 28, 401 (1895); 30, 1248 (1897); Hoff, *Ann. Chem.*, 311, 102 (1895).

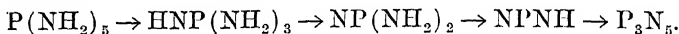
Equations (2) and (3) represent, in principle, the action of aquo nitric acid on aniline to form a phenyl aquo-ammono nitrate.

Phenylnitramide is very susceptible to the action of aqueous acids. However instead of undergoing hydrolytic decomposition to aniline and nitric acid it is converted largely into o-nitraniline and in lesser degree into p-nitraniline,  $C_6H_5NHNO_2 \rightarrow H_2NC_6H_4NO_2$ . When heated with potassium hydroxide at  $230^\circ$  to  $290^\circ$  phenylnitramide is hydrolyzed to potassium nitrate and aniline while at the same time potassium nitrite and other products are formed. Under the action of sodium amalgam or zinc dust phenylnitramide is reduced successively to diazobenzene, phenylhydrazine and finally to aniline and ammonia. The reactions involved are strictly similar to those concerned in the familiar reduction of nitric acid to nitrous acid and finally to ammonia.

## CHAPTER XVI.

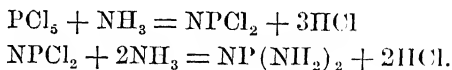
### AMMONO AND AQUO-AMMONO PHOSPHORIC AND PHOSPHOROUS ACIDS.

**Ammono Phosphoric Acids.** Running more or less closely parallel to the known series of aquo phosphoric acids one might expect to find an analogous series of ammono phosphoric acids as represented herewith,

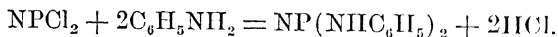


As a matter of fact three deammonation products of an hypothetical phosphoric pentamide are known, namely, phosphoric nitride diamide,  $\text{NP}(\text{NH}_2)_2$ , phospham,  $\text{NP}(\text{NH})$ , and phosphoric nitride  $\text{P}_3\text{N}_5$ .

*Phosphoric Nitride-diamide*,  $\text{NP}(\text{NH}_2)_2$ . According to Besson and Rosset<sup>1</sup> this ammono phosphoric acid is formed by the action of liquid ammonia on phosphoric nitride-chloride.<sup>2</sup> Just as water converts phosphorus pentachloride successively into phosphorus oxide-chloride and orthophosphoric acid, so as first observed by Liebig and Wöhler,<sup>3</sup> ammonia acts on phosphorus pentachloride to form phosphoric nitride-chloride, which, according to Besson and Rosset, is converted to phosphoric nitride-diamide by the further action of ammonia. The ammonolytic reactions involved are represented by the equations,



No metallic salts of this ammono phosphoric acid have been prepared. Several esters, however, are known, among them a diphenyl ester<sup>4</sup> which has been obtained by the action of aniline on phosphorus nitride-chloride as represented by the equation,



<sup>1</sup> Besson and Rosset, *Compt. rend.*, **146**, 1149 (1908).

<sup>2</sup> No analyses are given.

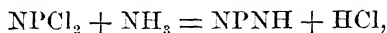
<sup>3</sup> Liebig and Wöhler, *Ann. Chem.*, **11**, 146 (1834).

<sup>4</sup> Hofmann, *Ber.*, **17**, 1911 (1884). Cf. Couldridge, *J. Chem. Soc.*, **53**, 40 (1888).

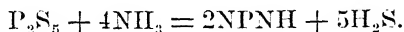
By the action of aqueous hydrochloric acid at  $250^{\circ}$  this ester is hydrolyzed to aquo phosphoric acid, aniline and ammonia.

*Phospham*,  $\text{N}\equiv\text{P}\cdot\text{NH}$ . This compound, first obtained by Davy<sup>5</sup> by heating phosphorus pentachloride in an atmosphere of ammonia and believed by the discoverer, by Rose, and by Liebig and Wöhler<sup>6</sup> to be a nitride of phosphorus, was shown by Gerhardt<sup>7</sup> to have the composition represented by the above formula.

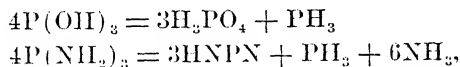
Phospham, which is the name given this ammono phosphoric acid by Gerhardt, is also obtained by heating phosphoric nitride-diamide,  $\text{NP}(\text{NH}_2)_2 \rightleftharpoons \text{NPNH} + \text{NH}_3$ , by heating a mixture of trimolecular nitride-chloride, and ammonium chloride,<sup>8</sup>



and by heating phosphorus pentasulfide with ammonium chloride,<sup>9</sup>

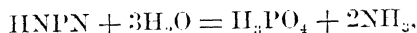


According to Rose<sup>10</sup> phospham is obtained when the product of the action of ammonia on phosphorus trichloride is strongly heated. This formation of an ammono phosphoric acid from an ammono phosphorous acid by the action of heat reminds one of the analogous conversion of aquo phosphorous acid into aquo phosphoric acid under similar treatment. While apparently Rose did not note the formation of phosphine as a product of his reaction we may nevertheless venture to write the equations,



to represent the parallel reactions.

Phospham is known in the form of a white, infusible powder, insoluble in water or dilute acids and only slowly attacked by aqueous potassium hydroxide. It is undoubtedly a highly polymerized substance. When heated with water in a sealed tube it is hydrolyzed in accordance with the equation.



<sup>5</sup> Davy, *Gilb. Ann.*, **39**, 6 (1811).

<sup>6</sup> Liebig and Wöhler, *Ann. Chem.*, **11**, 139 (1839).

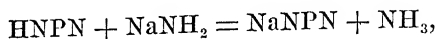
<sup>7</sup> Gerhardt, *Ann. chim. phys.*, [3] **188** (1846); **20**, 255 (1847). Cf. Besson, *Compt. rend.*, **114**, 1266 (1892).

<sup>8</sup> Couldridge, *J. Chem. Soc.*, **53**, 398 (1888).

<sup>9</sup> Vidal, *Chem. Zentralb.*, 1897, II, 517.

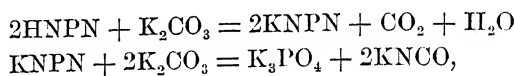
<sup>10</sup> Rose, *Pogg. Ann.*, **24**, 308 (1832); **28**, 529 (1833).

to orthophosphoric acid and ammonia. It dissolves readily in fused sodium amide with the evolution of ammonia. The melt, which undoubtedly contains a sodium ammonophosphate formed surmisedly in accordance with the equation,



on treatment with water gives a solution containing sodium aquophosphate.<sup>11</sup>

Observations by Vidal<sup>12</sup> on the formation of potassium aquophosphate and potassium cyanate by the action of fused potassium carbonate on phospham are readily explained when this compound is recognized as an ammono phosphoric acid. The reactions involved may be represented by the equations,



in accordance with which the ammono phosphoric acid acts on potassium aquocarbonate setting free carbonic anhydride and forming an ammonophosphate of potassium. This salt reacts with potassium aquocarbonate to form potassium aquophosphate and an aquo-ammono-carbonate of potassium, which is to say that in principle the ammonophosphate is hydrolyzed to the aquophosphate the aquo-carbonate at the same time undergoing ammonolysis to the aquo-ammono-carbonate.

By the action of methyl alcohol on hot phospham Vidal obtained methylamine and dimethylamine presumably in accordance with the equation,



which in principle, represents the hydrolysis of an ammono phosphoric acid to an aquo phosphoric acid and the ammonolysis of aquo methyl alcohol to the two ammono methyl alcohols.

Phospham and formic acid when heated together yield aquo phosphoric acid and hydrocyanic acid in a manner which may be represented by the equation,  $\text{NPNH} + 2\text{HCOOH} = \text{H}_3\text{PO}_4 + 2\text{HCN}$ . Clearly the ammono phosphoric acid undergoes hydrolysis to aquo phosphoric acid while aquo formic acid is at the same time ammonolyzed to formic anammonide. So also are other carboxylic acids converted into their respective nitriles when heated with phospham.

<sup>11</sup> Unpublished observations.

<sup>12</sup> Vidal, *Chem. Zentr.*, 1897, II, 517; 1899, I, 960; 1900, I, 743.

**Aquo-ammono Phosphoric Acids.** Twenty-five or more compounds, the existence of some of which as chemical individuals is doubtful, are described and classified by Gutbier<sup>13</sup> as amido, imido and nitrilo derivatives of ortho, pyro, tri, tetra and hepta phosphoric acids and of the polymeric forms of metaphosphoric acid. Some of these acids are known in the free state, others in the form of salts only while certain of them exist in the form of esters.

It will be worth while to discuss here only a few of the simpler of these compounds with the object in view of showing that they are to be looked upon as mixed aquo-ammono phosphoric acids.

**Amido Ortho Phosphoric Acid,**  $\text{H}_2\text{N-PO}(\text{OH})_2$ , is known in the free state as well as in the form of salts, esters and ester-salts. Examples of some of these compounds are represented by the following formulas,

- (1)  $\text{H}_2\text{N-PO}(\text{OC}_2\text{H}_5)_2$
- (2)  $(\text{C}_2\text{H}_5)_2\text{N-PO}(\text{OH})_2$ ,
- (3)  $\text{C}_6\text{H}_5\text{NH-PO}(\text{OC}_2\text{H}_5)_2$ ,
- (4)  $(\text{C}_6\text{H}_5)_2\text{N-PO}(\text{OC}_2\text{H}_5)_2$ ,
- (5)  $\text{H}_2\text{N-PO}(\text{OAg})\text{OC}_2\text{H}_5$ ,

all of which on hydrolysis yield aquo phosphoric acid. In addition to aquo phosphoric acid the first compound yields ammonia and ethyl alcohol, the second, diethylamine, the third, aniline and ethyl alcohol, the fourth, diphenylamine and ethyl alcohol. The ester-salt (5) yields aquo phosphoric acid, ammonia, ethyl alcohol and silver oxide.

**Diamido Ortho Phosphoric Acid,**  $(\text{H}_2\text{N})_2\text{PO-OH}$ . This acid is known in the free state and in the form of salts, esters and ester-salts. Three esters and an ester-salt of this acid are represented by the formulas, (1)  $(\text{CH}_3)_2\text{N-P}(\text{OH})\text{NH}_2$ , (2)  $(\text{C}_6\text{H}_5\text{NH})_2\text{PO-OH}$ , (3)  $[(\text{C}_2\text{H}_5)_2\text{N}]_2\text{PO-OC}_2\text{H}_5$ , (4)  $(\text{C}_6\text{H}_5\text{NH})_2\text{PO-OAg}$ .

In view of the fact that neither of the acids represented by the formulas,  $\text{P}(\text{OH})_5$  and  $\text{P}(\text{NH}_2)_5$ , is known it is interesting to note in this connection that Stokes,<sup>14</sup> starting with diamido ortho phosphoric acid, prepared a number of salts, among them the silver compounds represented by the formulas,  $(\text{H}_2\text{N})_2\text{P}(\text{OAg})_3$ ,  $(\text{AgNH})_2\text{-P}(\text{OAg})_3$  and  $\text{H}_2\text{N-P}(\text{NHAg})_2(\text{OAg})_2$ , which he called salts of the diamide and the triamide of pentabasic phosphoric acid. Other derivatives of the hypothetical phosphorus pentahydroxide represented by the formulas,  $(\text{C}_6\text{H}_5\text{NH})_3\text{P}(\text{OH})_2$ ,<sup>15</sup>  $\text{HO-P}(\text{NHC}_6\text{H}_4\text{SO}_2\text{OH})_4$ <sup>16</sup> and  $\text{Cl-P}(\text{NHC}_6\text{H}_5)_4$ ,<sup>16</sup> have been prepared.

<sup>13</sup> Gmelin-Kraut, "Handb. anorg. Chem." 7th Ed., I, 3, 215 (1911).

<sup>14</sup> Stokes, *Am. Chem. J.*, 16, 140 (1894).

<sup>15</sup> Michaelis and Silberstein, *Ber.*, 29, 721 (1896).

<sup>16</sup> Gilpin, *Am. Chem. J.*, 19, 357, 361 (1897).

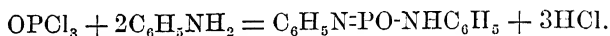


Lemoult<sup>17</sup> obtained several compounds which he looked upon as derivatives of pentabasic phosphoric acid. It may well be that phosphorus exists in these compounds with a covalence of five.<sup>18</sup>

*Triamido Ortho Phosphoric Acid*,  $\text{OP}(\text{NH}_2)_3$ . The existence of this acid is not certain. Nor are metallic salts of the acid known. Esters represented by the formulas,  $\text{OP}[\text{N}(\text{C}_2\text{H}_5)_2]_3$ ,<sup>19</sup>  $\text{OP}(\text{NHC}_6\text{H}_5)_3$ ,<sup>20</sup> and  $\text{OP}[\text{N}(\text{C}_2\text{H}_5)(\text{C}_6\text{H}_5)]_3$ , are however recorded in the literature.

*Ortho Phosphoric Acid Amide-imide, Phosphamide*,  $\text{OP}(\text{NH})\text{-NH}_2$ . This mixed aquo-ammono phosphoric acid has been obtained as an insoluble powder by the action of aqua ammonia on phosphorus pentachloride. It is converted by the action of fused potassium hydroxide into potassium orthophosphate and ammonia. Hot water hydrolyzes it slowly to ortho phosphoric acid and ammonia. When heated it loses ammonia and is converted into phosphoric anhydride-anammonide,  $\text{OPN}$ .

Esters of this mixed acid are known. For example a compound named oxyphosphazobenzene anilide,  $\text{C}_6\text{H}_5\text{N=PO-NHC}_6\text{H}_5$ , has been prepared by the action of aniline on phosphorus oxychloride,<sup>21</sup>



Gutbier<sup>22</sup> gives data concerning the methods of preparation and some of the properties of some sixteen amido, imido and nitrilo derivatives of di-, tri-, tetra- and hepta phosphoric acids some of which are known in the free state, the majority in the form of salts only. Apparently none is known as an ester.

*Aquo-ammono Metaphosphoric Acids*,  $\text{H}_2\text{NPO}_2$ . By the action of water on the respective nitride-chlorides,  $(\text{NPOCl}_2)_3$ ,  $(\text{NPOCl}_2)_4$ ,  $(\text{NPOCl}_2)_5$ , and  $(\text{NPOCl}_2)_6$ , Stokes<sup>23</sup> has obtained aquo-ammono phosphoric acids represented by the formulas,  $(\text{H}_2\text{NPO}_2)_3$ ,  $(\text{H}_2\text{NPO}_2)_4$ ,  $(\text{H}_2\text{NPO}_2)_5$ , and  $(\text{H}_2\text{NPO}_2)_6$ . Stokes also prepared metallic salts of certain of these acids. Michaelis<sup>24</sup> prepared the N-N-diethyl ester of trimolecular amido metaphosphoric acid,  $[(\text{C}_2\text{H}_5)_2\text{NPO}_2]_3$ .

*Ammono Phosphorous Acids, Phosphorous Amide*,  $\text{P}(\text{NH}_2)_3$ , *Phosphorous Imide-amide*,  $\text{HN=P-NH}_2$ , *Phosphorous Imide*,  $\text{HN=P-NH-P-NH}$ . Just as water acts on the phosphorous halides to

<sup>17</sup> Lemoult, *Compt. rend.*, **139**, 409 (1904); **141**, 1241 (1905).

<sup>18</sup> Lewis, "Valence and the Structure of Atoms and Molecules," p. 101, A. C. S. Monograph, New York, Chemical Catalog Co., Inc., 1923.

<sup>19</sup> Michaelis, *Ann. Chem.*, **326**, 200, 257 (1903).

<sup>20</sup> Michaelis and Soden, *Ann. Chem.*, **229**, 335 (1885).

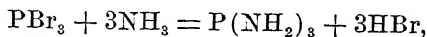
<sup>21</sup> Michaelis and Silberstein, *Ber.*, **29**, 717 (1896).

<sup>22</sup> Gmelin-Kraut, 7th Ed., I, **3**, 226 (1911).

<sup>23</sup> Stokes, *Am. Chem. J.*, **18**, 629, 780 (1896); **20**, 740 (1898).

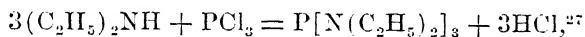
<sup>24</sup> Michaelis, *Ann. Chem.*, **326**, 190 (1903).

form phosphorous acid so, as reported by Hugot,<sup>25</sup> phosphorous amide is formed in accordance with the equation,

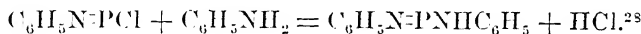


by the action, at  $-70^\circ$ , of liquid ammonia on phosphorus tribromide while according to Joannis,<sup>26</sup> phosphorous imide-amide is obtained when phosphorus trichloride vapor, diluted with hydrogen, is passed into liquid ammonia at  $-78^\circ$ . Both observers agree that their respective products lose ammonia and pass over into phosphorous imide,  $\text{P}_2(\text{NH})_3$ , when warmed to  $0^\circ$ . Whether by further loss of ammonia phosphorous imide may be converted into phosphorous anammonide,  $\text{PN}$ , is unknown. These ammono phosphorous acids are the phosphorus analogs of the hypothetical ammono nitrous acids,  $\text{N}::(\text{NH}_2)_3$ ,  $\text{H}_2\text{N}::\text{N}::\text{NH}$  and  $\text{HN}::\text{N}::\text{NH}::\text{N}::\text{NH}$ , which are discussed later (*cf.* Chapter XXXI). No metallic salts of these ammono phosphorous acids have been prepared.

**Ammono Phosphorous Acid Esters.** Attempts to prepare metallic salts of an ammono phosphorous acid have not been made. Two examples of ammono phosphorous acid esters, known respectively as phosphorous acid tris-diethyl amide and phosphazobenzene-anilide, are represented by the formulas,  $[(\text{C}_2\text{H}_5)_2\text{N}]_3\text{P}$  and  $\text{C}_6\text{H}_5\text{N}=\text{P}=\text{NHC}_6\text{H}_5$ . The one has been obtained by the action of phosphorus trichloride on diethylamine,



the other, by the action of aniline on a phosphorous acid ester-chloride known as phosphazobenzene chloride,



The first compound is clearly an ester of ortho ammono phosphorous acid, the second of an ammono phosphorous acid of the formula,  $\text{HN}=\text{P}=\text{NH}_2$ . Both esters are hydrolyzed by the action of aqueous hydrochloric acid, the one to aquo phosphorous acid and diethylamine, the other to aquo phosphorous acid and aniline. The second ester may be looked upon as diazoaminobenzene in which nitrous acid nitrogen is replaced by phosphorous acid phosphorus.

<sup>25</sup> Hugot, *Compt. rend.*, **141**, 1235 (1905).

<sup>26</sup> Joannis, *Compt. rend.*, **139**, 365 (1904); *cf.* Perpérot, *Bull. soc. chim.*, [4] **37**, 1545 (1925).

<sup>27</sup> Michaelis, *Ann. Chem.*, **326**, 169 (1903).

<sup>28</sup> Michaelis and Schroeter, *Ber.*, **27**, 494 (1894).

**Aquo-ammonio Phosphorous Acids.** Three aquo-ammonio phosphorous acids are represented by the formulas,  $\text{HO-P}(\text{NH}_2)_2$ ,  $(\text{HO})_2\text{P-NH}_2$  and  $\text{O-P-NH}_2$ . The first has been prepared by the action of ammonia on phosphorous anhydride in ether solution.<sup>29</sup> The other two are known in the form of esters only.

Two esters of the first acid formulated above are represented by the formulas,  $\text{C}_2\text{H}_5\text{O-P}=[\text{N}(\text{C}_2\text{H}_5)_2]_2$ <sup>30</sup> and  $\text{HO-P}(\text{NHC}_6\text{H}_5)_2$ ,<sup>31</sup> one of the second by the formula,  $(\text{C}_6\text{H}_5\text{O})_2\text{P-N}(\text{C}_4\text{H}_9)_2$ ,<sup>30</sup> and two of the third by the formulas  $\text{C}_6\text{H}_5\text{O-P-NC}_6\text{H}_5$ <sup>31</sup> and  $\text{C}_6\text{H}_5\text{CH}_2\text{O-P-NC}_6\text{H}_5$ .<sup>32</sup>

**Aquo-ammonio Vanadic, Arsenic and Antimonic Acids.** By the action of liquid ammonia on vanadic anhydride, on arsenic acid anhydride and on antimony pentachloride Jacobsohn<sup>33</sup> obtained products which are to be looked upon as ammonium salts of an aquo-ammonio vanadic acid, an aquo-ammonio arsenic acid and an aquo-ammonio antimonic acid.

<sup>29</sup> Thorpe and Tutton, *J. Chem. Soc.*, 59, 1027 (1890).

<sup>30</sup> Michaelis, *Ann. Chem.*, 326, 161 (1903).

<sup>31</sup> Jackson and Menke, *Am. Chem. J.*, 6, 93 (1884-85).

<sup>32</sup> Michaelis and Schroeter, *Ber.*, 27, 495 (1894).

<sup>33</sup> Felix Jacobsohn, *Inaug. Diss.*, Berlin, 1906.

## CHAPTER XVII.

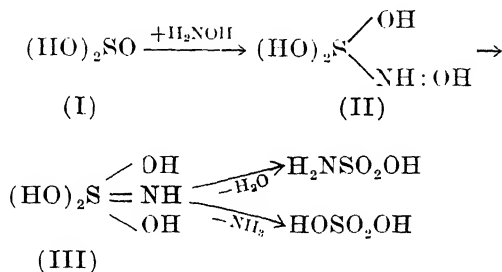
### AQUO-AMMONO SULFURIC ACIDS.

Attempts made in this laboratory to prepare some one or other of the hypothetical ammonia analogs of aquo-ammonio sulfuric acid represented by the formulas,  $S(NH_2)_6$ ,  $HN-S(NH_2)_4$ ,  $N\equiv S(NH_2)_3$ ,  $S(NH)_3$ , or of a sulfuric anammonide,  $SN_2$ , have not been successful. Nor are there any compounds on record which may be interpreted as derivatives of an ammonio sulfuric acid.

It happens, however, that compounds in considerable number are known which are to be looked upon as aquo-ammonio sulfuric acids.

**Amido Sulfuric Acid,**<sup>1</sup>  $H_2N-SO_2-OH$ , is a strong monobasic acid<sup>2</sup> which is formed in small quantity by the action of ammonia on sulfuric anhydride,  $SO_3 + NH_3 = H_2NSO_2OH$ , and in excellent yield by heating fluo sulfuric acid in the form of its ammonium salt with strong aqua ammonia,  $FSO_2OH + NH_3 = H_2NSO_2OH + HF$ .<sup>3</sup>

Amido sulfuric acid is also formed, together with more or less sulfuric acid, by the action of hydroxylamine hydrochloride on sulfur dioxide or on acid sodium sulfite.<sup>4</sup> It is reasonable to suppose that the action of hydroxylamine on sulfurous acid takes place stepwise as represented by the scheme,



<sup>1</sup> The compounds represented by the formulas,  $H_2NSO_2OH$ ,  $HN(SO_2OH)_2$  and  $N(SO_2OH)_3$ , are generally known as amido sulfonic acid, imido sulfonic acid and nitrilo sulfonic acid respectively. The use of these names is unfortunate for the reason that neither of the first two of these compounds is a sulfonic acid, nor is the last one a nitrile, in the accepted connotation of these terms. Compounds represented by the formulas,  $RSO_2OH$  and  $RCN$ , in which R is an alkyl or aryl radical, are sulfonic acids and nitriles respectively. The above-formulated compounds are sulfuric acids.

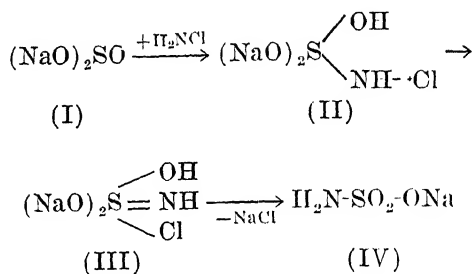
<sup>2</sup> The amido hydrogen atoms are weakly acid.

<sup>3</sup> Traube and Brehmer, *Ber.*, **52**, 1272 (1919).

<sup>4</sup> Raschig, "Schwefel- und Stickstoffstudien," Leipzig-Berlin, 1924.

in accordance with which an hypothetical sulfurous acid oxime (II) is first formed. This unknown hydroxamic acid undergoing intramolecular rearrangement, identical in principle with the Beckmann transformation, passes over into an aquo-ammono sulfuric acid (III) which in turn either loses water to form amido sulfuric acid or rearranges to ammonium sulfate. Of course there is no specific experimental evidence in support of these speculations beyond experience to the effect that many oximes undergo the Beckmann rearrangement and the well-known fact that many acids react with hydroxylamine to form hydroxamic acids.

Sodium amidosulfate is obtained in good yield by the interaction of chloramine and disodium sulfite.<sup>5</sup> It is probable that the reactions involved take place in a manner more or less adequately represented by the scheme,



It is assumed that disodium aquesulfite (I) unites with chloramine to form a salt of an aquo-ammono sulfurous ammono hypochlorous acid (II) which undergoing a Hofmann-like rearrangement is converted into (III) which is a sodium salt and at the same time a chloride of an aquo-ammono sulfuric acid. Such a compound should lose sodium chloride to form sodium amidosulfate (IV).

*Metallic Salts.* Many metallic salts of this half amide of sulfuric acid are known, among others for example, a monopotassium salt,  $\text{H}_2\text{N}\cdot\text{SO}_2\text{OK}$ , a dipotassium salt,  $\text{KH}\text{N}\cdot\text{SO}_2\text{OK}$ , a mercuric salt,  $(\text{HgN}\cdot\text{SO}_2\text{O})_2\text{Hg}\cdot 4\text{H}_2\text{O}$ , a potassium silver salt,  $\text{AgH}\text{N}\cdot\text{SO}_2\text{OK}$ , a sodium mercury salt,  $\text{HgN}\cdot\text{SO}_2\text{ONa}$ , a potassium gold salt,  $\text{Au}_2(\text{N}\cdot\text{SO}_2\text{OK})_3$ , and a potassium aquobasic mercuric salt,  $\text{HOHg}\cdot\text{N}(\text{hg})\cdot\text{SO}_2\text{OK}$ .<sup>6</sup>

*Esters and Ester-Salts.* Examples of esters and ester-salts of amido sulfuric acid are represented by the following formulas,  $\text{C}_2\text{H}_5\text{NH}\cdot\text{SO}_2\text{OH}$ ,  $(\text{CH}_3)_2\text{NSO}_2\text{OH}$ ,  $(\text{CH}_3)_2\text{NSO}_2\text{OC}_2\text{H}_5$ ,  $\text{C}_2\text{H}_5\text{NH}\cdot\text{SO}_2\cdot$

<sup>5</sup> Raschig, "Schwefel- und Stickstoffstudien," 1924.

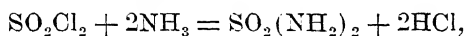
<sup>6</sup> Divers and Haga, *J. Chem. Soc.*, 69, 1649 (1896); Berglund, *Bull. soc. chim.*, [2] 27, 452 (1876); [2] 29, 422 (1878).

OK,  $(C_6H_5)(CH_3)NSO_2OK$ ,  $(C_2H_5NHSO_2O)_2Ca \cdot 2H_2O$ . and  $(C_2H_5NHSO_2O)_2Pb$ .<sup>7</sup>

**Imido Sulfuric Acid**,  $NH(SO_2OH)_2$ . This aquo-ammono sulfuric acid is known in the free state in water solution and in the form of metallic salts. Examples selected from a known list of twenty or more of such salts are the following,  $KN(SO_2OK)_2 \cdot H_2O$ ,  $AgN(SO_2OAg)_2$ ,  $Ca[N(SO_2O)_2Ca]_2$ ,  $NaN(SO_2O)_2Ba$ ,  $Pb[N(SO_2O)_2Pb]_2$ ,  $AgN(SO_2ONa)_2$ ,  $AgN(SO_2OAg)(SO_2ONa)$ , a basic strontium salt,  $HOSrN(SO_2OSrOH)_2$ , a basic lead salt,  $HOPbN(SO_2OPbOH)_2$ , and a basic mercuric salt,  $HOHgN(SO_2OHg)_2O$ .<sup>8</sup>

**Nitrido Sulfuric Acid**,  $N(SO_2OH)_3$ , is an aquo sulfuric acid and at the same time a sulfuric acid nitride. It is a sulfuric anammonide in so far as the relationship between sulfur and nitrogen is concerned. It is known in the form of salts only.

**Sulfamide**,  $SO_2(NH_2)_2$ .<sup>9</sup> This aquo-ammono sulfuric acid is formed in small yield by the action of ammonia on sulfuryl chloride in accordance with the equation,



which represents the ammonolysis of a sulfuric oxide-chloride to an aquo-ammono sulfuric acid. Much better yields are obtained by the action of ammonia on sulfuryl fluoride.<sup>10</sup> Sulfamide is a crystalline solid. It dissolves abundantly in water and in liquid ammonia to form solutions which are very poor, though distinct, conductors of electricity.<sup>11</sup> Heated in aqueous acid solution it undergoes hydrolysis first to amido sulfuric acid and thence to aquo sulfuric acid. When heated alone it yields deammonation products among which imido disulfamide,  $H_2N-SO_2-NH-SO_2-NH_2$ , and trimolecular sulfamide,  $(SO_2NH)_3$ , have been identified.

**Metallic Salts.** That sulfamide has the properties of an acid is shown by the existence of a considerable number of metallic salts. Traube<sup>12</sup> prepared the disilver salt,  $SO_2(NHAg)_2$ , by the action of ammoniacal silver nitrate on an aqueous solution of sulfamide. Franklin and Stafford<sup>13</sup> obtained impure specimens of the mono- and dipotassium salts,  $H_2NSO_2NHK$  and  $SO_2(NHK)_2$ , by the action of potassium amide on sulfamide in liquid ammonia solution. Sodium and potassium salts of the formulas,  $H_2NSO_2NHNa$  and

<sup>7</sup> Behrend, *Ber.*, 15, 1613 (1882); Beilstein and Wiegand, *Ber.*, 16, 1264 (1883); Traube and Brehmer, *Ber.*, 52, 1291 (1919).

<sup>8</sup> Divers and Haga, *J. Chem. Soc.*, 61, 943 (1892); 69, 1620 (1896).

<sup>9</sup> Any one of the further tautomeric formulas,  $H_2N(NH)SO_2OH$ ,  $(HN)_2S(OH)_2$ , or  $NS(NH_2)(OH)_2$ , may be written for this compound.

<sup>10</sup> Traube and Reubke, *Ber.*, 56, 1656 (1925).

<sup>11</sup> Hantzsch and Stuer, *Ber.*, 38, 1022 (1905); Franklin, *Z. physik. Chem.*, 69, 272 (1909).

<sup>12</sup> Traube, *Ber.*, 26, 609 (1893).

<sup>13</sup> Franklin and Stafford, *Am. Chem. J.*, 28, 83 (1902).

$\text{H}_2\text{NSO}_2\text{NHK}$ , are formed by the action of the respective alkali metal alcoholates on sulfamide in alcohol solution, the lithium salt,  $\text{H}_2\text{NSO}_2\text{NHLi}$ , by adding alcohol to a water solution containing equivalent quantities of sulfamide and lithium hydroxide, the barium salt,  $(\text{H}_2\text{NSO}_2\text{NH})_2\text{Ba}$ , contaminated with barium amidosulfate, by dissolving barium hydroxide in a water solution of sulfamide; the copper salt,  $(\text{H}_2\text{N-SONH})_2\text{Cu.4NH}_3$ , by dissolving cupric hydroxide in a strong aqua ammonia solution of sulfamide and adding alcohol to the solution of the salt thus formed.<sup>14</sup>

*Esters.* Alkyl and aryl derivatives of sulfamide,<sup>15</sup> such for example as symmetrical and unsymmetrical dimethylsulfamide,  $\text{CH}_3\text{-NHSO}_2\text{NHCH}_3$  and  $(\text{CH}_3)_2\text{NSO}_2\text{NH}_2$ , tetraethylsulfamide,  $(\text{C}_2\text{H}_5)_2\text{-NSO}_2\text{N}(\text{C}_2\text{H}_5)_2$ , and the dimethylphenyl derivative of the formula,  $(\text{CH}_3)_2\text{NSO}_2\text{NHC}_6\text{H}_5$ , are to be looked upon as esters of this aquo-ammonio sulfuric acid. N-N-Dimethyl-N'-phenylsulfamide, which is formally an acid ester, has been found to react with sodium hydroxide in water solution to form a sodium salt,  $(\text{CH}_3)_2\text{NSO}_2\text{N}(\text{Na})\text{-C}_6\text{H}_5$ . O-Esters of sulfamide are not known.

*Imido Disulfamide*,  $\text{H}_2\text{NSO}_2\text{-NH-SO}_2\text{-NH}_2$ , which is an aquo-ammonio disulfuric acid, has been identified among the products formed by the interaction of sulfuryl chloride and ammonia.<sup>16</sup> It is known in the free state and in the form of an ammonium salt,  $\text{NH}_3\text{.IIN}(\text{SO}_2\text{NH}_2)_2$ , a monosilver salt,  $\text{AgN}(\text{SO}_2\text{NH}_2)_2\text{.1}\frac{1}{2}\text{H}_2\text{O}$ , and, according to Ephraim and Michel, a trisilver salt,  $\text{AgN}(\text{SO}_2\text{NHAg})_2\text{.xH}_2\text{O}$  containing water in amounts from three to not less than forty-six molecules.<sup>17</sup>

From the mixture of products formed by the action of sulfuryl chloride on an excess of ammonia Ephraim and Michel obtained an aquo-ammonio trisulfuric acid in the form of its trisilver salt,  $\text{AgHN-SO}_2\text{-NAg-SO}_2\text{-NH-SO}_2\text{-NHAg.NH}_3\text{.5}\frac{1}{2}\text{H}_2\text{O}$ , and a tetrasulfuric acid in the form of a hexasilver salt,  $\text{Ag}_2\text{N-SO}_2\text{-NAg-SO}_2\text{-NI-SO}_2\text{-NAg-SO}_2\text{-NAg}_2$  (with  $1\frac{1}{2}$ , 11 and 28  $\text{H}_2\text{O}$ ), and a heptasilver salt,  $\text{Ag}_2\text{N-SO}_2\text{-NAg-SO}_2\text{-NAg-SO}_2\text{-NAg-SO}_2\text{-NAg}_2\text{.8H}_2\text{O}$ . Excepting for their water content Ephraim and Michel were inclined to the belief that the above formulas represent definite compounds though at the same time admitting that the products analyzed may possibly have been mixtures.

It is interesting to observe the parallelism between the formal deammonation of urea successively to di-, tri-, tetra- and pentacarbonic acids,  $\text{H}_2\text{N-CO-NH}_2 \rightarrow \text{H}_2\text{N-CO-NH-CO-NH}_2 \rightarrow \text{H}_2\text{N-CO-NH-}$

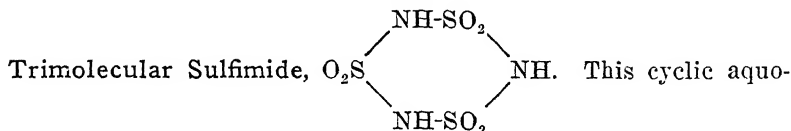
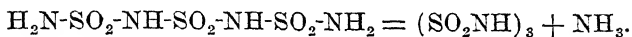
<sup>14</sup> Traube and Reubke, *Ber.*, 56, 1656 (1923).

<sup>15</sup> Franchimont, *Rec. trav. chim.*, 3, 418 (1884); Behrend, *Ann. Chem.*, 222, 116 (1884).

<sup>16</sup> Traube, *Ber.*, 25, 2472 (1892); 26, 607 (1893); Hantzsch and Holl, *ibid.*, 34, 3430 (1901); Hantzsch and Stuer, *ibid.*, 38, 1022 (1905).

<sup>17</sup> Ephraim and Michel, *Ber.*, 42, 3833 (1909); Ephraim and Gurewitsch, *ibid.*, 43, 138 (1919).

$\text{CO-NH-CO-NH}_2 \rightarrow \text{H}_2\text{N-CO-NH-CO-NH-CO-NH-CO-NH}_2 \rightarrow \text{H}_2\text{N-CO-NH-CO-NH-CO-NH-CO-NH-CO-NH}_2$  and the similar stepwise deammonation of sulfamide,  $\text{H}_2\text{N-SO}_2\text{-NH}_2 \rightarrow \text{H}_2\text{N-SO}_2\text{-NH-SO}_2\text{-NH}_2 \rightarrow \text{H}_2\text{N-SO}_2\text{-NH-SO}_2\text{-NH-SO}_2\text{-NH}_2 \rightarrow \text{H}_2\text{N-SO}_2\text{-NH-SO}_2\text{-NH-SO}_2\text{-NH-SO}_2\text{-NH}_2$ , to di-, tri- and tetra-sulfuric acids. This is not to say, however, that such reactions have been experimentally realized excepting that biuret and cyanuric acid are among the products formed by heating urea and that imido-disulfamide and trimolecular sulfimide are formed when sulfamide is heated. It is furthermore known that triuret is readily deammonated to cyanuric acid,  $\text{H}_2\text{N-CO-NH-CO-NH-CO-NH}_2 = (\text{OCNH})_3 + \text{NH}_3$ , and that trimolecular sulfimide is probably formed by loss of ammonia from the open chain trisulfuric acid in the same manner,



ammono trisulfuric acid is present among the products formed by the action of ammonia on sulfuryl chloride and is also formed by heating sulfamide. It is a fairly strong acid of which the silver salts,  $(\text{SO}_2\text{NAg})_3$  and  $(\text{SO}_2\text{NAg})_3 \cdot 6\text{C}_5\text{H}_5\text{N}$  ( $\text{C}_5\text{H}_5\text{N} = \text{pyridine}$ ), the potassium  $(\text{SO}_2\text{NK})_3$ , sodium  $(\text{SO}_2\text{NNa})_3$ , calcium  $(\text{SO}_2\text{Nca})_3$ , and barium  $(\text{SO}_2\text{Nba})_3 \cdot \text{H}_2\text{O}$  salts have been prepared. Traube prepared also the lead and copper salts but did not analyze them. The free acid is known only in solution.

By the action of methyl iodide on the silver salt of trisulfimide Hantzsch and HOLL obtained the N-N'-N''-trimethyl derivative of trisulfimide,  $(\text{SO}_2\text{NCH}_3)_3$ , the one ester of this acid which has been prepared. On heating the ester with concentrated hydrochloric acid at a temperature of  $150^\circ$  it is hydrolyzed in accordance with the equation,  $(\text{SO}_2\text{NCH}_3)_3 + 3\text{H}_2\text{O} = 3\text{H}_2\text{SO}_4 + 3\text{CH}_3\text{NH}_2$ , to methylamine and sulfuric acid.

**Aquo-Ammono-Chromates, Molybdates and Tungstates.** Using liquid ammonia as solvent in which to carry out the reactions involved Jacobsohn<sup>18</sup> prepared an ammonium salt,  $\text{HN}=\text{CrO}(\text{ONH}_4)_2$ , a potassium salt,  $\text{KN}=\text{CrO}(\text{OK})_2$ , a potassium ammonium salt,  $\text{HN}=\text{CrO}(\text{OK})(\text{ONH}_4)$ , an ammonium lead salt,  $[\text{HN}=\text{CrO}(\text{ONH}_4)_2\text{O}]_2\text{Pb}$ , of an aquo-ammono chromic acid, an ammonium salt,  $\text{HN}=\text{MoO}(\text{ONH}_4)_2$  and an ammonium lead salt,  $[\text{HN}=\text{MoO}(\text{ONH}_4)_2\text{O}]_2\text{Pb}$ , of an aquo-ammono molybdic acid, and an ammonium salt,  $\text{HN}=\text{WO}(\text{ONH}_4)_2$ , salt of an aquo-ammono tungstic acid.

<sup>18</sup> Felix Jacobsohn, Inaug. Diss., Berlin, 1906.



## CHAPTER XVIII.

### AMMONO SULFUROUS ACID, AMMONO-THIO SULFURIC ACID, AQUO-AMMONO SULFUROUS ACID AND SULFACYLIC ACID.

**Ammono Sulfurous Acid and Ammono-Thio Sulfuric Acid.** While no one of the theoretically possible ammono sulfurous acids represented by the formulas,  $S(NH_2)_4$ ,  $HNS(NH_2)_2$  or  $NSNH_2 \rightleftharpoons HNSNH$ , nor an ammono-thio sulfuric acid is known it is interesting to find that Ruff and Geisel,<sup>1</sup> in the course of an investigation undertaken to determine the constitution of tetrasulfur tetranitride, obtained two compounds of the empirical composition represented by the formulas,  $H_3N_3SHg$  and  $H_3N_3S_2Pb$ , which they named thiodiimide mercury and dithiodiimide lead respectively.

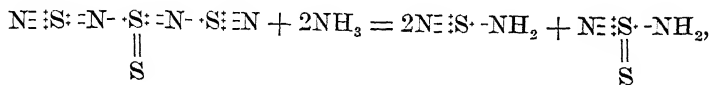
A comparison of the formula of Ruff and Geisel's thiodiimide mercury with the formulas given above shows that this compound has the composition of a mercury salt either of the ammono sulfurous acid,  $HNS(NH_2)_2$ , or of an ammonated salt of the acid,  $NSNH_2$  or  $HNSNH$ . The hypothetical acid from which dithiodiimide lead is derived differs in empirical composition from the ammono sulfurous acid of which thiodiimide mercury is a salt in that it contains, relative to the nitrogen content, twice as much sulfur. This relation is just that which exists between oxygen and sulfur in ordinary sulfurous acid on the one hand and thio sulfuric acid on the other. It therefore appears that dithiodiimide lead may be a salt of an ammono-thio sulfuric acid of the formula,  $HN=S_2(NH_2)_2$ , or an ammonated salt of an acid represented by either of the formulas,  $N=S_2-NH_2$  or  $HN S_2 NH$ . The following discussion based on the work of Ruff and Geisel lends convincing support to the view above developed concerning the nature of these compounds.

**Mercuric Ammonosulfite,  $NES-NHg.NH_3$ , and Lead Ammono-thio-sulfate,  $N=S_2-N=Pb.NH_3$ .** Ruff and Geisel found that a yellow precipitate of the former compound is formed when mercuric iodide is added to a liquid ammonia solution of sulfur nitride and that a precipitate of dithiodiimide lead is obtained when lead iodide is used as precipitant.

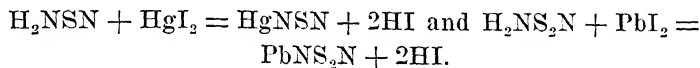
These observations are readily explained on the assumptions first,

<sup>1</sup> Ruff and Geisel, *Ber.*, 37, 1573 (1904).

that sulfur nitride is a mixed sulfurous thio sulfuric anammonide which in liquid ammonia solution is ammonated to a mixture of an ammono sulfurous acid and an ammono-thio sulfuric acid as represented by the equation,



and second, that mercuric thiodiimide, happening to be insoluble, is precipitated when mercuric iodide is added to the solution while lead dithiodiimide, being likewise insoluble, is precipitated in the presence of lead iodide. The respective reactions involved may be represented by the equations,<sup>2</sup>



A third assumption is of course to the effect that thiodiimide lead and dithiodiimide mercury, both of which remain unknown, are soluble in liquid ammonia.

The presence of ammono-thio sulfuric acid in the solution from which the mercuric ammonosulfite had been precipitated and filtered was shown by the formation of a precipitate of lead ammono-thio-sulfate when lead iodide was added to the filtrate. In a similar manner mercuric iodide added to the solution from which the ammono-thio sulfuric acid had been removed in the form of its lead salt, gave a precipitate of mercuric ammonosulfite.

Our assumption that in liquid ammonia solution sulfur nitride is ammonated to a mixture of ammono sulfurous acid and ammono-thio sulfuric acid in the proportion of two molecules of the former to one of the latter is in harmony with Ruff and Geisel's observations to the effect that the highest yield of thiodiimide mercury is obtained when two molecules of mercuric iodide are used per molecule of sulfur nitride while the best yield of dithiodiimide lead results when sulfur nitride and lead iodide are brought together in equimolecular proportions.

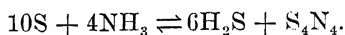
Ruff and Geisel further observed that when a liquid ammonia solution of sulfur nitride is evaporated to dryness, which is to say to the complete removal of liquid ammonia, a residue of the empirical composition  $\text{S}_4\text{N}_4 \cdot 2\text{NH}_3$ , is obtained which on warming is converted into sulfur nitride. This ammonated product may have been

<sup>2</sup> It is immaterial for present purposes which of the formulas,  $\text{NSNHg} \cdot \text{NH}_2$  or  $\text{HN}(\text{NH})\text{SNHg}$  on the one hand and  $\text{NS}_2\text{NPb} \cdot \text{NH}_2$  or  $\text{H}_2\text{N}(\text{NH})\text{S}_2\text{NPb}$ , on the other, may be ascribed to the respective salts.

either a mixture of ammonio sulfurous acid and ammonio-thio sulfuric acid,  $2\text{NSNH}_2 \cdot \text{NS}_2\text{NH}_2$ , as has been assumed above or perhaps a mixed ammonio sulfurous ammonio-thio sulfuric acid, say of the formula,  $\text{H}_2\text{N}(\text{NH})\text{S}-\text{N}-\text{S}_2-\text{N}-\text{S}(\text{NH})\text{NH}_2$ , which on treatment with mercuric iodide breaks down to form mercuric ammonosulfite and ammonio-thio sulfuric acid, while in the presence of lead iodide it yields lead ammonio-thio-sulfate and ammonio sulfurous acid.

**The Action of Liquid Ammonia on Sulfur and of Hydrogen Sulfide on Sulfur Nitride in Liquid Ammonia Solution.** When silver iodide in liquid ammonia solution is added to a solution of sulfur in the same solvent six-tenths of the sulfur is recovered in the form of insoluble silver sulfide. Then on evaporating the filtrate from the silver sulfide thus precipitated, and warming the residue left behind, a mixture of ammonium iodide and sulfur nitride is obtained, the latter in an amount accounting for the remaining four-tenths of the sulfur used.<sup>3</sup> On the other hand, by dissolving sulfur nitride in liquid ammonia, adding to the solution thus formed somewhat more than six molecular equivalents of hydrogen sulfide and evaporating away the solvent together with the excess of hydrogen sulfide (ammonium sulfide), Ruff and Geisel obtained ten atoms of elementary sulfur for each molecule of tetrasulfur tetranitride used.

Dispensing for the moment with any surmises concerning the mechanism of the reactions involved it will be clear that first and last the action of ammonia on sulfur and of hydrogen sulfide on sulfur nitride may be represented by the reversible equation,



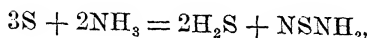
On the one hand hydrogen sulfide and sulfur nitride are formed by the interaction of sulfur and ammonia, on the other sulfur and ammonia result from the action of hydrogen sulfide in sulfur nitride. The equilibrium represented by this equation is displaced completely to the right when, as was done by Ruff and Geisel, the hydrogen sulfide is removed from the system by means of silver iodide. It is displaced to the left when the liquid ammonia is allowed to evaporate away.

It will be recalled that potassium hydroxide, in water solution, acts on sulfur to form potassium sulfides and potassium thiosulfate together with salts of a number of other thio acids. Ignoring the polysulfides and the thio acid salts other than thiosulfate we may represent the reactions involved in the formation of the sulfide and the thiosulfate as follows,  $3\text{S} + 6\text{KOH} = 2\text{K}_2\text{S} + \text{K}_2\text{SO}_3 + 3\text{H}_2\text{O}$ , and  $\text{K}_2\text{SO}_3 + \text{S} = \text{K}_2\text{S}_2\text{O}_3$ . The first equation shows that two sulfur atoms out of three undergo reduction to the dinegative state,

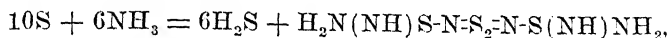
<sup>3</sup> Ruff and Geisel, *Ber.*, **38**, 2659 (1905).

the third being simultaneously augmented to sulfurous acid sulfur. In the presence of sulfur potassium sulfite is converted into potassium thiosulfate. Similar reactions apparently take place, although very sluggishly, when sulfur is heated with water. Assuming now that liquid ammonia resembles water, or even aqueous potassium hydroxide, in its action on sulfur then the experimental observations of Ruff and Geisel outlined above find at least a partial explanation as follows.

Sulfur in liquid ammonia solution undergoes simultaneous augmentation and reduction in accordance with the equation,



to form hydrogen sulfide (ammonium sulfhydrate) and ammono sulfurous acid which latter compound then reacts with sulfur to form ammono-thio sulfuric acid,  $NSNH_2 + S = NS_2NH_2$ . Equilibrium is established, we will say, in accordance with the equation,



as the result of the formation of an ammono sulfurous ammono-thio sulfuric acid.

**Hydrolysis of Sulfur Nitride.** If sulfur nitride is a sulfurous thio sulfuric anammonide it might be expected to undergo hydrolytic decomposition to aquo sulfurous acid, aquo-thio sulfuric acid and ammonia. As a matter of fact, as shown by Ruff and Geisel, the major products formed by the action of aqueous potassium hydroxide on sulfur nitride are potassium sulfite, potassium thiosulfate and ammonia. In principle the reactions involved are represented by the equation,  $N_4S_4 + 9H_2O = 2H_2SO_3 + H_2S_2O_3 + 4NH_3$ .

Other observations by Ruff and Geisel, which need not be recalled here, are in entire harmony with the view that sulfur nitride, thiodiimide mercury and dithiodiimide lead are respectively a mixed sulfurous thio sulfuric anammonide, a mercuric ammono-sulfite and a lead ammono-thio-sulfate. None is in disagreement. No esters of ammono sulfurous acid nor of ammono-thio sulfuric acid are known.

**Aquo-Ammono Sulfurous Acids.** Compounds of the respective formulas,  $H_2NSO_2H$ ,  $H_2NSO_2NH_4$ ,  $NH_4.N(SO_2NH_4)_2$  and  $N_4H_{12}S_5O_{10}$ , have been isolated from the products formed by the interaction of sulfur dioxide and ammonia.<sup>4</sup> The first and second formulas represent an aquo-ammono unisulfurous acid and its ammonium salt respectively, the third represents the tri-ammonium salt of an aquo-ammono disulfurous acid,  $HN(SOOH)_2$ , while the

<sup>4</sup> Divers and Ogawa, *J. Chem. Soc.*, 77, 327 (1900); 79, 1099 (1901); Schumann, *Z. anorg. Chem.*, 23, 43 (1900); Ephraim and Piotrowski, *Ber.*, 44, 379 (1911).

fourth, if given the formula,  $\text{HO-SO-NH-SO-NH-SO-NH-SO-NH-SO-OH} \cdot 3\text{H}_2\text{O}$  represents a hydrated aquo-ammono pentasulfurous acid. Compare with formula for a hepta silver aquo-ammono tetrasulfate on page 170.

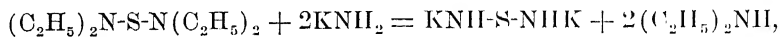
According to Ephraim and Piotrowski a sulfurous acid diamidimide of the formula  $\text{HN}(\text{SONH}_2)_2$ , is formed by the action of liquid ammonia on thionyl chloride albeit the existence of such an aquo-ammono disulfurous acid was not confirmed by analysis.

In addition to the ammonium salts mentioned above salts of aquo-ammono sulfurous acids represented by the formulas,  $\text{IIN}(\text{SO}_2\text{-NH}_4)_2$ ,  $\text{HN}(\text{SO}_2\text{K})_2$ , and  $\text{AgN}(\text{SOAg})_2$ , have been prepared.

*Esters.* Many compounds have been prepared by the action of thionyl chloride and of sulfur dioxide on the amines which are to be regarded as esters of aquo-ammono sulfurous acids. For example, thionylaniline,  $\text{C}_6\text{H}_5\text{NSO}$ ,<sup>5</sup> and thionyl-diethylamine,  $[(\text{C}_2\text{H}_5)_2\text{N}]_2\text{SO}$ ,<sup>6</sup> which have been obtained by the action of thionyl chloride on aniline and on diethylamine, are esters of two unknown aquo-ammono sulfurous acids of the formulas,  $\text{IINSO}$  and  $\text{IIN-SO-NH}_2$ , while the compounds,  $\text{C}_2\text{H}_5\text{NH-SO-OH}$ <sup>7</sup> and  $(\text{CH}_3)_2\text{NSO}_2\text{H}$ ,<sup>8</sup> obtained by the action of sulfur dioxide on ethylamine and on dimethylamine respectively, are esters of the aquo-ammono sulfurous acid,  $\text{H}_2\text{NSO}_2\text{H}$ , which, as noted above, is among the products formed by the interaction of ammonia and sulfur dioxide.

These esters and others of their kind are readily hydrolyzed by the action of water, aqueous acids or alkalis to amines (ammono alcohols) and sulfurous anhydride.

**Ammono Sulfoxylic Acid, Sulfazylic Acid,  $\text{S}(\text{NH}_2)_2$ .** Esters of this nitrogen analog of an unknown sulfoxylic acid,  $\text{S}(\text{OH})_2$ ,<sup>9</sup> have been prepared by the action of secondary amines on sulfur dichloride, a tetraethyl ester for example, in accordance with the equation,  $\text{SCl}_2 + 2(\text{C}_2\text{H}_5)_2\text{NH} = (\text{C}_2\text{H}_5)_2\text{N-S-N}(\text{C}_2\text{H}_5)_2 + 2\text{HCl}$ .<sup>10</sup> More recently Clark<sup>11</sup> has obtained a potassium salt of sulfazylic acid by the action of potassium amide on tetraethyl sulfazylate in liquid ammonia solution. The equation,



represents the saponification of the ester to form the dipotassium salt of the acid and an ammono ethyl alcohol.

<sup>5</sup> Michaelis and Herz, *Ber.*, **24**, 745 (1891).

<sup>6</sup> Michaelis and Schindler, *Ber.*, **28**, 1016 (1895).

<sup>7</sup> Michaelis and Storbeck, *Ann. Chim.*, **274**, 192 (1893).

<sup>8</sup> Schumann, *Z. anorg. Chem.*, **23**, 61 (1900).

<sup>9</sup> Vogel and Partington, *J. Chem. Soc.*, **127**, 1522 (1925); Bassett and Durant, *J. Chem. Soc.*, **130**, 1407 (1927).

<sup>10</sup> Lengfeld and Stieglitz, *Ber.*, **28**, 575 (1895); Michaelis, *Ber.*, **28**, 1016 (1895).

<sup>11</sup> C. K. Clark, Thesis, Stanford University, 1929.

## CHAPTER XIX.

### AMMONO HYPOCHLOROUS ACIDS.

We come now to inquire concerning the existence of ammono acids derived from the elements of the seventh periodic group. Selecting chlorine as a typical halogen we may write formulas for hypothetical nitrogen analogs of hypochlorous acid, chlorous acid, chloric acid and perchloric acid as follows,  $\text{H}_2\text{NCl}$  and  $\text{HNCl}_2$ , for two ammono hypochlorous acids,  $\text{H}_2\text{NCINH}$ , for an ammono chlorous acid,  $\text{HNCIN}$ , for an ammono chloric acid and  $\text{H}_2\text{NCIN}_2$ , for an ammono perchloric acid. Of the compounds thus formulated only two are known, namely, monochloramine and dichloramine; the first in the free state and in the form of esters,  $\text{RHNCl}$  and  $\text{RRNCl}$ , the other in solution<sup>1</sup> and in the form of esters,  $\text{RNCl}_2$ . The remaining purely hypothetical compounds may well be incapable of existence.

**Ammono Hypochlorous Acids, Monochloramine,  $\text{H}_2\text{N} \cdot \text{Cl}$ , and Dichloramine,  $\text{HN} \cdot \text{Cl}_2$ .** Monochloramine is obtained by the action of aqua ammonia on a water solution of sodium hypochlorite.<sup>2</sup> According to Raschig the reaction takes place as represented by the equation,  $\text{NaOCl} + \text{NH}_3 = \text{H}_2\text{NCl} + \text{NaOH}$ , which in principle may be written,  $\text{HO} \cdot \text{Cl} + \text{NH}_3 = \text{H}^2\text{N} \cdot \text{Cl} + \text{H}_2\text{O}$ , and read as involving the ammonolysis of aquo hypochlorous acid to an ammono hypochlorous acid.

The pure compound has been obtained in the form of colorless crystals by passing the mixed vapors of chloramine and water over potassium carbonate and condensing the dried product at liquid air temperature.<sup>3</sup> Monochloramine melts at  $-66^\circ$  and decomposes at a somewhat higher temperature.

*Hydrolysis of Monochloramine.* We have just learned that Raschig obtained monochloramine by the ammonolysis of aquo hypochlorous acid. Inversely in accordance with observations of Marckwald and Wille monochloramine is hydrolyzable to aquo hypochlorous acid and ammonia. In one set of experiments these investigators found that ammonia is formed when the mixed vapors of monochloramine and water are passed over soda-lime and in another that dichlorine oxide is obtained by passing the mixed vapors

<sup>1</sup> Chapin, *J. Am. Chem. Soc.*, **51**, 2112 (1929).

<sup>2</sup> Raschig, *Z. anorg. Chem.*, **20**, 2068 (1907); *Ber.*, **40**, 4586 (1907); *Chem. Ztg.*, **31**, 126 (1907).

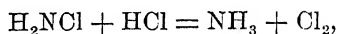
<sup>3</sup> Marckwald and Wille, *Ber.*, **56**, 1319 (1923).

over calcium chloride. Assuming that the reactions represented by the equation,  $\text{H}_2\text{N-Cl} + \text{H}_2\text{O} \rightleftharpoons \text{HO-Cl} + \text{NH}_3$ , are reversible it follows that the aquo hypochlorous acid resulting from the hydrolysis of chloramine is fixed by the soda-lime leaving the ammonia unacted upon.<sup>5</sup> The formation of dichlorine oxide and the non-appearance of ammonia in the second set of experiments are readily explained on the assumption that the dichlorine oxide is formed by the dehydration of the aquo hypochlorous acid and that the ammonia is fixed by the calcium chloride as ammonia of crystallization.

*Deammonation of Monochloramine.* Aquo hypochlorous acid may be dehydrated to hypochlorous anhydride by distilling its aqueous solution under diminished pressure<sup>6</sup> while the acid is reformed by dissolving the anhydride in water.

According to Marckwald and Wille, the analogous deammonation of monochloramine to hypochlorous anammonide takes place spontaneously when it is allowed to stand in contact with water, the reaction involved probably taking the stepwise course represented as follows,  $2\text{ClNH}_2 = \text{Cl}_2\text{NH} + \text{NH}_3$ ,  $3\text{Cl}_2\text{NH} = 2\text{Cl}_3\text{N} + \text{NH}_3$ . The inverse ammonation of trichlorine nitride to monochloramine has not been definitely established.

*Action of Hydrochloric Acid on Monochloramine.* Just as hydrochloric acid is familiarly known to act on aquo hypochlorous acid yielding water and free chlorine so similarly, according to Raschig, it acts on monochloramine as represented by the equation,



to form ammonia and chlorine. Noyes<sup>7</sup> has shown that hydrochloric acid acts on chlorine nitride in an entirely similar manner,  $\text{NCl}_3 + 3\text{HCl} = 3\text{Cl}_2 + \text{NH}_3$ . He states furthermore that the reactions probably take place with the intermediate formation of dichloramine and monochloramine. Whether chlorine nitride is hydrolyzable to aquo hypochlorous acid and ammonia is apparently unknown.

*Action of Chlorine on Ammonia.* Aquo hypochlorous acid is formed by the action of chlorine on water,<sup>8</sup> one-half of the chlorine thereby undergoing reduction to chlorine ions, the other half augmentation to unipositive chlorine, or, what amounts to much the

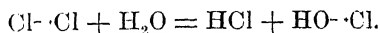
<sup>5</sup> Whether the ammonio hypochlorous acid reacts with water as represented above or with one of the constituents of the soda-lime, say sodium hydroxide in accordance with the equation,  $\text{H}_2\text{NCl} + \text{NaOH} = \text{NaOCl} + \text{NH}_3$ , is a matter of indifference in the present connection since both reactions are, in principle, hydrolytic.

<sup>6</sup> Goldschmidt, *Ber.*, 52, 753 (1919).

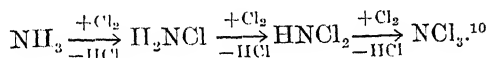
<sup>7</sup> W. A. Noyes, *J. Am. Chem. Soc.*, 42, 2173 (1920).

<sup>8</sup> Jakowin, *Z. physik. Chem.*, 29, 613 (1899).

same thing, one may say that elementary chlorine, regarded as potentially a hypochlorous acid chloride, is hydrolyzed by the action of water to hypochlorous hydroxide and hydrochloric acid,



According to Marckwald and Wille<sup>9</sup> chlorine acts on ammonia in a similar manner to form trichlorine nitride and hydrochloric acid. The reactions involved probably take place stepwise as represented by the scheme,



*Decomposition of Monochloramine.* Nitrogen, ammonia, hydrochloric acid, hydrogen, hydrazine and hydrazoic acid have been identified among the products formed by the decomposition of monochloramine under different conditions.<sup>11</sup>

In explanation of the manner in which monochloramine decomposes in alkaline solution to form the products enumerated Raschig makes a good case in support of the following assumptions.

The primary reaction consists in the decomposition of chloramine in accordance with the equation,  $\text{NH}_2\text{Cl} = \text{NH} + \text{HCl}$ , just as aquo hypochlorous acid breaks down to form oxygen and hydrochloric acid.<sup>12</sup> The free imide group thus formed reacts in at least three ways, the relative speeds of the three reactions varying with conditions. First, some of the imido groups break down to form hydrogen and nitrogen, (1)  $2\text{NH} = \text{N}_2 + \text{H}_2$ , second, others augment (nitridize) ammonia to hydrazine, (2)  $\text{NH}_3 + \text{NH} = \text{H}_3\text{N}:\text{NH}$ , while still others polymerize to triimide, (3)  $3\text{NH} = (\text{NH})_3$ , which for the most part decomposes to form nitrogen and ammonia, (4)  $(\text{NH})_3 = \text{N}_2 + \text{NH}_3$ , and to a lesser extent is augmented by the action of chloramine to hydrazoic acid, (5)  $(\text{NH})_3 + \text{NH}_2\text{Cl} =$

<sup>9</sup> Marckwald and Wille, *Ber.*, **56**, 1319 (1923).

<sup>10</sup> Bray and Dowell, *J. Am. Chem. Soc.*, **39**, 905 (1917); Noyes, *J. Am. Chem. Soc.*, **42**, 2173 (1920); Gattermann, *Ber.*, **21**, 753 (1888).

<sup>11</sup> Raschig, "Schwefel- und Stickstoffstudien," 1924.

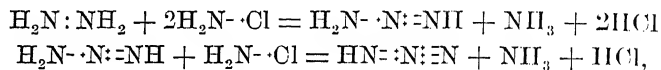
<sup>12</sup> Stock [*Ber.*, **53**, 839 (1920)] thinks it probable that the decomposition of chloramine into nitrogen, ammonia and hydrochloric acid takes place as represented by the equations, (a)  $3\text{NH}_2\text{Cl} = \text{NCl}_3 + 2\text{NH}_3$ , (b)  $\text{NCl}_3 + \text{NH}_3 = \text{N}_2 + 3\text{HCl}$ . Clearly equation (a) represents the deammonation of an ammono hypochlorous acid to hypochlorous anammonide. If we follow Stock it is interesting to observe that equation (b) may be interpreted as consisting in the ammonolysis of a possible tautomeric form of chlorine nitride, that is to say of a nitrous acid chloride, to nitrous anammonide and hydrochloric acid,  $\text{NCl}_3 + 3\text{NH}_3 = \text{N}(\text{NH}_2)_3 + 3\text{HCl}$ . It is assumed that an ammono nitrous acid is formed which undergoes deammonation,  $\text{N}(\text{NH}_2)_3 = \text{N}_2 + 2\text{NH}_3$ , to form nitrous anammonide which of course appears as nitrogen.



$\text{HN}=\text{N}=\text{N} + \text{NH}_3 + \text{HCl}$ . The reaction represented by equation (1) becomes conspicuous when the decomposition of chloramine is brought about at elevated temperatures. In accordance with equation (2) hydrazine is formed by the action of the free imide group on ammonia. This nitridation of ammonia to hydrazine is analogous to the oxidation of water to hydrogen peroxide.

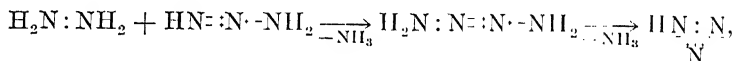
Raschig's assumption of the formation of a trimer of the imide group, equation (3), is interesting for the reason that this short-lived compound instead of being assigned a cyclic formula as was done by Raschig may just as well, probably rather, be looked upon as an ammono nitrous acid which would be expected to break down to ammonia and nitrogen,  $\text{HN}=\text{N} \cdot \text{N} \cdot \text{NH}_2 = \text{N}_2 + \text{NH}_3$ , or to undergo augmentation in accordance with the equation,  $\text{HN}=\text{N} \cdot \text{N} \cdot \text{NH}_2 + \text{NH} = \text{HN}=\text{N}:\text{N}=\text{N} + \text{NH}_3$ , to form ammono nitric acid.<sup>13</sup>

Recalling that hydrazine is among the products of the decomposition of chloramine in alkaline solution it may well be that hydrazoic acid is formed in accordance with some such equations as



which represent the nitridation of hydrazine first to ammono nitrous acid and thence to ammono nitric acid.

Finally, since hydrazoic acid is undoubtedly a tautomeric compound, its formation may alternately be explained on the assumption that ammono nitrous acid (Raschig's triimide) acts on hydrazine as represented by the equation,



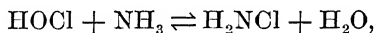
to form a cyclic nitrous acid hydrazide.

*Monochloramine as an Augmenting Agent.* Using the terms oxidation and nitridation each in its specific sense it follows that just as aquo hypochlorous acid is well known to be an efficient oxidizing agent so analogously monochloramine should function as a nitridizing agent. The primary augmenting agent in both aquo and ammono hypochlorous acids is, of course, the hypochlorous acid chlorine with its strong tendency to acquire electrons. When ordinary hypochlorous acid decomposes in accordance with the equation,  $\text{HO} \cdot \text{Cl} = \text{HCl} + \text{O}$ , the dinegative oxygen is robbed of two electrons thereby becoming a powerful oxidizing agent, while similarly

<sup>13</sup> Of course it is not known whether the augmenting agent is chloramine, the free imide group, aquo hypochlorous acid or nascent oxygen.

when ammono hypochlorous acid decomposes as represented by the equation,  $\text{H}_2\text{N} \cdot \text{Cl} = \text{HCl} + \text{NH}$ , the imide group thus formed may be regarded as an analogous nitridizing agent.

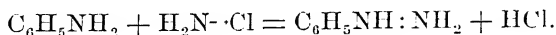
In an entirely reasonable sense both aquo hypochlorous acid and chloramine may be said to act as chloridizing agents and indeed the use of such an expression is sometimes helpful as, for example, when one speaks of the intramolecular transformation of phenyl hypochlorite into chlorphenol and of phenylchloramine into chloraniline as consisting in the chloridizing action of the hypochlorous acid chlorine contained in the respective hypochlorites. It is obvious in view of the reversibility of the equation,



that water solutions of monochloramine may be expected to show either oxidizing or nitridizing properties or indeed both simultaneously.

The formation of sulfuric acid from sulfur dioxide and of potassium cyanate from potassium cyanide by the action of chloramine in water solution and the very considerable yield of potassium chlorate obtained by warming monochloramine with fairly concentrated potassium hydroxide solution<sup>14</sup> are probably best accounted for on the assumption that aquo hypochlorous acid, resulting from the hydrolysis of chloramine, is the active agent.

On the other hand Short<sup>15</sup> obtained potassium dicyanamide,  $\text{KN}(\text{CN})_2$ , by the action of an aqueous solution of monochloramine on potassium cyanide, a result which is to be interpreted as involving the conversion of an ammonocarbonite into an ammonocarbonate by the nitridizing action of an ammono hypochlorous acid. Raschig<sup>16</sup> observed the formation of phenylhydrazine as a product of the action of monochloramine on aniline,



Obviously ammonia nitrogen is augmented to hydrazine nitrogen while concomitantly hypochlorous acid chlorine is reduced to hydrochloric acid chlorine.

Not enough is known of the bromine and iodine derivatives of ammonia to make it worth while to consider them here.

**Esters of Ammono Hypochlorous Acids.** Assuming the chloram-

<sup>14</sup> Raschig, *Z. ang. Chem.*, **20**, 2068 (1907); *Chem. Ztg.*, **31**, 126 (1907); *Ber.*, **40**, 4586 (1907). Marekwald and Wille, *Ber.*, 1319 (1923).

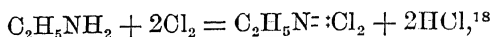
<sup>15</sup> Short, *Chem. News*, **126**, 100 (1925).

<sup>16</sup> Raschig, *Z. anorg. Chem.*, **20**, 2068 (1907).

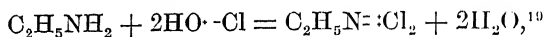
ines established as ammonio hypochlorous acids it follows that their alkyl derivatives represented by the formulas,  $\text{RNH}\cdot\text{Cl}$ ,  $\text{R}_2\text{N}\cdot\text{Cl}$  and  $\text{RN}::\text{Cl}_2$ , are to be regarded as ammonio hypochlorous acid esters.

*Ethylchloramine*,  $\text{C}_2\text{H}_5\text{NH}\cdot\text{Cl}$ , and *Diethylchloramine*,  $(\text{C}_2\text{H}_5)_2\text{N}\cdot\text{Cl}$ , have been obtained by the action of sodium hypochlorite on the hydrochlorides of ethylamine and diethylamine respectively.<sup>17</sup> The equations,  $\text{C}_2\text{H}_5\text{NH}_2 + \text{HO}\cdot\text{Cl} = \text{C}_2\text{H}_5\text{NH}\cdot\text{Cl} + \text{H}_2\text{O}$ , and  $(\text{C}_2\text{H}_5)_2\text{NH} + \text{HO}\cdot\text{Cl} = (\text{C}_2\text{H}_5)_2\text{N}\cdot\text{Cl} + \text{H}_2\text{O}$ , in accordance with which the respective reactions take place, represent typical esterification reactions.

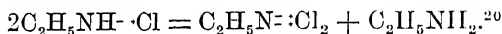
*Ethylidichloramine*,  $\text{C}_2\text{H}_5\text{N}::\text{Cl}_2$ , has been prepared (1) by passing chlorine into an aqueous solution of ethylamine,



(2) by the action of chlorinated lime on ethylamine hydrochloride,



and (3) by the action of dilute sulfuric acid on ethylchloramine,



The first equation may be said to represent the formation of an ethyl ammoniohypochlorite by the action of hypochlorous acid chloride,  $\text{Cl}\cdot\text{Cl} \rightleftharpoons \text{Cl}\cdot\text{Cl}$ , on an ammonio alcohol. According to the second equation an ethyl ammoniohypochlorite is formed by the action of aquo hypochlorous acid on an ammonio ethyl alcohol. The third equation represents the interaction of two molecules of an acid ester to form one molecule each of a neutral ester and an alcohol.

The alkylchloramines are ill-smelling yellowish liquids which decompose more or less readily on standing excepting that some of the carefully purified dichloramines have been kept indefinitely.

**The Alkylchloramines as Augmenting Agents.** Like monochloramine the ammonio hypochlorous acid esters as active augmenting agents convert hydrogen sulfide to sulfur, sulfur dioxide to sulfuric acid and react with the halogen acids to liberate the free halogens.<sup>21</sup>

Berg found furthermore that aldehydes, presumably formaldehyde and acetaldehyde, and methylamine are formed by warming

<sup>17</sup> Berg, *Ann. chim.*, [7] 3, 319 (1894).

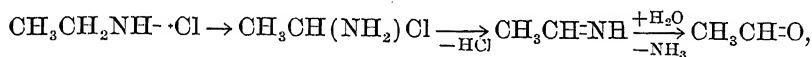
<sup>18</sup> Würtz, *Ann. chim. phys.*, [3] 30, 1474 (1849); *Ann. Chem.*, 76, 837 (1850).

<sup>19</sup> Tscherniak, *Ber.*, 9, 146 (1876); 32, 3582 (1899).

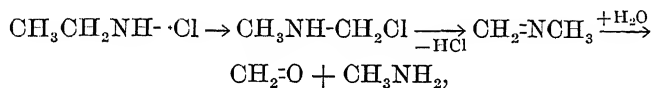
<sup>20</sup> Berg, *Ann. chim.*, [7] 3, 346 (1894).

<sup>21</sup> Berg, *Ann. chim. phys.*, [7] 337 (1894).

ethylchloramine in alcoholic potassium hydroxide solution and treating the mixture with excess of hydrochloric acid. The formation of acetaldehyde is explained on the assumption that intramolecular augmentation of the ethyl alcohol group and the simultaneous reduction of the hypochlorous acid chlorine takes place as follows,

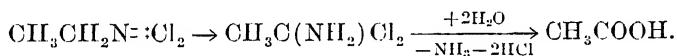


to form first the aldehyde amide-chloride which unstable compound loses hydrochloric acid to form ethylideneimine. This aldehyde-alcohol, in the presence of water, is hydrolyzed to acetaldehyde and ammonia. Methylamine and formaldehyde are formed as represented by the equation,



the hypochlorous acid chlorine attacking the carbon to carbon union.

The formation of acetic acid by the action of potassium hydroxide on ethyldichloramine as observed by Berg<sup>22</sup> involves the intramolecular augmentation of ethyl alcohol to acetic acid and the simultaneous reduction of hypochlorous acid chlorine to hydrochloric acid chlorine,



**Esters of Ammono Hypobromous Acids and of Ammono Hypoiodous Acids.** The alkyl bromamines and iodamines, in so far as they are known, resemble the alkylchloramines. They have been made by analogous processes, namely, by the action of the respective halogens and potassium hydroxide on aqueous solutions of salts of the amines, and also in certain instances by the direct action of the halogen on water solutions of the free amines.

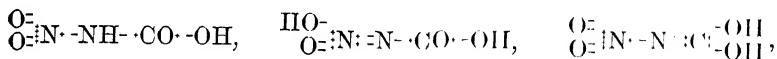
<sup>22</sup> Berg, *Ann. Chim. Phys.*, [7] 3, 343 (1894).

## CHAPTER XX.

### MIXED ACIDS.

We are already familiar with acids, such for example as diacetamide, dichloramine and dicyanamide, which are derivatives of ammonia containing two like acid-forming groups in place of two ammonia hydrogen atoms. Some examples of the many known acids of this type in which the imide group is attached to two unlike acid-forming groups are listed and briefly commented upon in this chapter.

To make clear our conception of the nature of these compounds we undertake to elucidate in some detail the structure of nitrocarbamic acid which is the first compound listed below.<sup>1</sup> As has already been shown (Chapter XV) nitramide is to be regarded as an aquo-ammono nitric acid to which any one of three tautomeric formulas may be ascribed. It is a nitric acid derived simultaneously from water and ammonia. It has also been shown in Chapter XI that carbamic acid, represented by either of the formulas,  $\text{H}_2\text{N} \cdot \text{CO} \cdot \text{OH}$  or  $\text{HN} \cdot \text{C} \equiv (\text{OH})_2$ , is an aquo-ammono carbonic acid. Writing the formulas,



for nitrocarbamic acid it appears that this compound is to be looked upon as a mixed aquo-ammono carbonic aquo-ammono nitric acid.

In speaking of nitrocarbamic acid as an aquo-ammono carbonic aquo-ammono nitric acid we are simply describing the compound in terms of the nomenclature adopted for use in this monograph and not giving it what would be a very cumbersome name.

**Carbonic-Nitric Acids.** Nitrocarbamic acid, which is known in the form of its potassium salt,  $\text{O}_2\text{N-NH-CO OK}$ , and nitrourea,  $\text{H}_2\text{N-CO-NH-NO}_2$ ,<sup>2</sup> are aquo-ammono carbonic aquo-ammono nitric

<sup>1</sup> In the opinion of the writer it would be better to confine the name nitro compounds to those compounds in which the  $\text{NO}_2$  group is in combination with carbon as in nitromethane since, properly speaking, neither nitramide nor nitrocarbamic acid is a nitro compound. Nitramide is a nitric acid while nitrocarbamic, as we shall see, is a mixed nitric-carbonic acid.

<sup>2</sup> Working with water solutions, Miss Jameson [Adelaide Jameson, Thesis, Stanford University, 1921] prepared the following salts of nitrourea,  $(\text{CH}_2\text{O}_2\text{N}_3)_2\text{Ca} \cdot \text{H}_2\text{O}$ ,  $(\text{CH}_2\text{O}_2\text{N}_3)_2\text{Ba} \cdot \text{H}_2\text{O}$ ,  $(\text{CH}_2\text{O}_2\text{N}_3)_2\text{Mg} \cdot \text{H}_2\text{O}$ ,  $(\text{CH}_2\text{O}_2\text{N}_3)_2\text{Cu} \cdot 5\text{H}_2\text{O}$ ,  $(\text{CH}_2\text{O}_2\text{N}_3)_2\text{Cu} \cdot 3\text{NH}_3$  and  $(\text{CH}_2\text{O}_2\text{N}_3)_2\text{Cd}$ .

acids. Nitroguanidine  $\text{H}_2\text{N}-\text{C}(\text{NH})\text{NH}-\text{NO}_2$ , is an ammono carbonic aquo-ammono nitric acid of which the silver salt,  $\text{H}_2\text{N}-\text{C}(\text{NH})\text{NAg}-\text{NO}_2$ , is known.

**Carbonic-Nitrous Acids.** Nitrosocarbamic acid,  $\text{ON}-\text{NH}-\text{CO}-\text{OH}$ , known in the form of esters, is an aquo-ammono carbonic aquo-ammono nitrous acid. Nitrosoguanidine,  $\text{H}_2\text{N}-\text{C}(\text{NH})\text{NH}-\text{NO}$ , is an ammono carbonic aquo-ammono nitrous acid. Cyantriazene,  $\text{HN}::\text{N}-\text{NH}-\text{CN}$ , known in the form of its phenyl ester and a phenyl ester silver salt, is an ammono carbonic ammono nitrous acid.

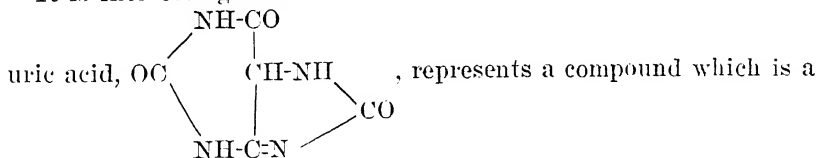
**Carbonic-Phosphoric Acids.** The formula,  $\text{H}_2\text{N}-\text{CO}-\text{NH}-\text{PO}(\text{OH})_2$ , represents an unknown aquo-ammono carbonic aquo-ammono phosphoric acid of which an ethyl ester,  $\text{H}_2\text{N}-\text{CO}-\text{NH}-\text{PO}(\text{OH})\text{OC}_2\text{H}_5$ , has been prepared.

**Carbonic-Sulfuric Acids.** Carbamidosulfuric acid,  $\text{H}_2\text{N}-\text{CO}-\text{NH}-\text{SO}_2\text{OH}$ , and carbamidodisulfuric acid,  $\text{O}-\text{C}(\text{NH}-\text{SO}_2-\text{OH})_2$ , are aquo-ammono carbonic aquo-ammono sulfuric acids. Dicyandiamidine-sulfuric acid,  $\text{H}_2\text{N}-\text{C}(\text{NH})\text{NH}-\text{CO}-\text{NH}-\text{SO}_2\text{OH}$ , is an aquo-ammono dicarbonic aquo-ammono sulfuric acid.

**Carbonic-Hypochlorous Acids.** Chlorurea,  $\text{H}_2\text{N}-\text{CO}-\text{NH}-\text{Cl}$ , is an aquo-ammono carbonic ammono hypochlorous acid.

**Carbonic-Carbylic Acids.** Acetylurea,  $\text{CH}_3\text{CO}-\text{NH}-\text{CO}-\text{NH}_2$ , diacetylurea,  $\text{CH}_3\text{CO}-\text{NH}-\text{CO}-\text{NH}-\text{OCCH}_3$ , acetylbiuret,  $\text{CH}_3\text{CO}-\text{NH}-\text{CO}-\text{NH}-\text{CO}-\text{NH}_2$ , and acetyldicyandiamidine,  $\text{CH}_3\text{CO}-\text{NH}-\text{C}(\text{NH})-\text{NH}-\text{CO}-\text{NH}_2$ , are aquo-ammono carbonic aquo-ammono acetic acids. Oxaluric acid,  $\text{H}_2\text{N}-\text{CO}-\text{NH}-\text{CO}-\text{CO}-\text{OH}$ , and parabanic acid, are respectively an open chain and a cyclic aquo-ammono oxalic aquo-ammono carbonic acid.

It is interesting to note that one of the tautomeric formulas for



mixed aquo-ammono carbonic aquo-ammono tartronic acid and at the same time, in respect to the  $-\text{C}(\text{NH})-\text{NH}-$  union, an N-ester of an aquo-ammono carbonic acid. Acetylguanidine,  $\text{CH}_3\text{CO}-\text{NH}-\text{C}(\text{NH})-\text{NH}_2$ , and acetylcyanamide,  $\text{CH}_3\text{CO}-\text{NH}-\text{CN}$ , are ammono carbonic aquo-ammono acetic acids. Benzoylcyanamide,  $\text{C}_6\text{H}_5\text{CO}-\text{NH}-\text{CN}$ , and dibenzoyldicyandiamide,  $(\text{C}_6\text{H}_5\text{CO}-\text{NH})_2\text{C}=\text{N}-\text{CN}$ , are ammono carbonic aquo-ammono benzoic acids.

**Carbonic-Sulfonic Acids.** Benzenesulfonylcarbamic acid,  $\text{C}_6\text{H}_5-\text{SO}_2\text{NH}-\text{CO}-\text{OH}$ , and benzenesulfonylurea,  $\text{C}_6\text{H}_5\text{SO}_2\text{NH}-\text{CO}-\text{NH}_2$ , are aquo-ammono carbonic aquo-ammono benzenesulfonic acids. Benzenesulfonylguanidine,  $\text{C}_6\text{H}_5\text{SO}_2\text{NH}-\text{C}(\text{NH})\text{NH}_2$ , and benzenesul-

fonylcyanamide,  $C_6H_5SO_2NH-CN$ , are ammono carbonic aquo-ammono benzenesulfonic acids.

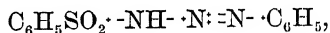
**Nitric-Sulfuric Acids.** Nitrosulfamide,  $H_2N-SO_2NH-NO_2$ , is an aquo-ammono nitric aquo-ammono sulfuric acid.

**Nitric-Sulfonic Acids.** Benzenesulfonnitramide,  $C_6H_5SO_2NH-NO_2$ , is an aquo-ammono nitric aquo-ammono benzenesulfonic acid of which Mathews<sup>3</sup> has prepared fourteen salts. Mathews also prepared metallic salts of p-toluenesulfonnitramide and of o-nitro-p-toluenesulfonnitramide.

**Nitrous-Carbylic Acids.** N-Nitrosoacetanilide,  $CH_3CO-N(NO)-C_6H_5$ , is a phenyl ester of an aquo-ammono nitrous aquo-ammono acetic acid. Benzoyldiazoaminobenzene,  $C_6H_5(C_6H_5CO)N=N-C_6H_5$ , is a diphenyl ester of an unknown ammono nitrous aquo-ammono benzoic acid,  $C_6H_5CO-N=N-NH_2$ .

Diazobenzenebenzamidine,  $C_6H_5C(NH)NH-N=N-C_6H_5$ , which is formed when benzenediazonium chloride and benzamidine are brought together in dilute sodium hydroxide solution, is an ester of an ammono nitrous ammono benzoic acid.<sup>4</sup>

**Nitrous-Sulfonic Acids.** A phenyl ester of an ammono nitrous aquo-ammono benzenesulfonic acid of the formula,



is known.

**Phosphoric-Carbylic Acids.** Benzoylphosphamic acid,  $C_6H_5CO-NH-PO(OH)_2$ , is an aquo-ammono phosphoric aquo-ammono benzoic acid.

**Sulfuric-Hypochlorous Acids.** Chloramidisulfuric acid,  $Cl-NH-SO_2OH$ , and monochlorosulfamide,  $H_2N-SO_2NH-Cl$ , are examples of aquo-ammono sulfuric ammono hypochlorous acids.

**Sulfuric-Carbylic Acids.** Benzoylamidosulfuric acid,  $C_6H_5CO-NH-SO_2OH$ , is an aquo-ammono sulfuric aquo-ammono benzoic acid. Benzamidinesulfuric acid,  $C_6H_5C(NH)NH-SO_2OH$ , is an aquo-ammono sulfuric ammono benzoic acid.

**Hypochlorous-Carbylic Acids.** Acetylchloramide,  $CH_3CO-NH-Cl$ , is an ammono hypochlorous aquo-ammono acetic acid.

**Hypochlorous-Sulfonic Acids.** Benzenesulfonylchloramide,  $C_6H_5SO_2NH-Cl$ , is an ammono hypochlorous aquo-ammono benzenesulfonic acid.

**Carbylic-Carbylic Acids.** Acetylbenzamide or benzoylacetamide,  $CH_3CO-NH-OCC_6H_5$ , is an aquo-ammono acetic aquo-ammonobenzoic acid. Acetylbenzamidine,  $C_6H_5C(NH)NH-OCC_6H_5$ , and diacetylbenzamidine,  $C_6H_5C(N-OCC_6H_5)NH-OCC_6H_5$ , are aquo-ammono acetic

<sup>3</sup> Mathews, *J. Phys. Chem.*, **24**, 108 (1920).

<sup>4</sup> Pinner, *Ber.*, **22**, 1609 (1889).

ammono benzoic acids. Benzoylbenzamidine,  $C_6H_5C(NH)NH-OCC_6H_5$ , is an ammono benzoic aquo-ammono benzoic acid.

**Carbylic-Sulfonic Acids.** Benzenesulfonylbenzamide,  $C_6H_5-SO_2NH-OCC_6H_5$ , is an example of an aquo-ammono benzoic aquo-ammono benzenesulfonic acid, benzenesulfonylbenzamidine,  $C_6H_5-SO_2-NH-(NH)CC_6H_5$ , of an ammono benzoic aquo-ammono benzene-sulfonic acid.



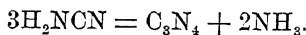
## CHAPTER XXI.

### ACID ANAMMONIDES.

Compounds related to the ammono acids as the acid anhydrides are related to the aquo acids we have chosen to call acid anammonides. The former are oxides, the latter are nitrides, of the non-metals and of negative or acid forming groups. Carbon dioxide and the oxide,  $(\text{CH}_3\text{C})_2\text{O}_3$ , for example, are respectively carbonic anhydride and acetic anhydride while carbonic nitride,  $\text{C}_3\text{N}_4$ , is a carbonic anammonide and acetoneitrile an acetic anammonide.

**Boric Anammonide,  $(\text{BN})_x$ .** Boron nitride is the nitrogen analog of boric anhydride and as such is to be regarded as an acid anammonide. It is formed by heating boron in an atmosphere of nitrogen and by heating boron imide,  $\text{B}_2(\text{NH})_3$ , which is an ammono boric acid. It is hydrolyzed by the action of water to aquo boric acid and ammonia.<sup>1</sup>

**Carbonic Anammonide,  $(\text{C}_3\text{N}_4)_x$ .** It might be expected that cyanamide, which is an ammono carbonic acid, on heating would lose ammonia and pass over into carbonic nitride in accordance with the equation,



Instead it undergoes polymerization to dicyandiamide and melamine. On further heating, the latter compound, losing ammonia, passes successively into melam and melem, two rather indefinitely characterized ammono carbonic acids, and finally into a yellow, insoluble, infusible product to which Liebig gave the name melon.

Years ago Schneider<sup>2</sup> found that carbonic nitride is formed as represented by the equation,



when cyanogen trisulfide is heated. However Schneider's compound has failed of record in the handbooks of chemistry and this, presumably, for the reason that in his paper adequate analytical data are wanting.

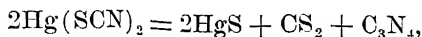
Investigations by Franklin<sup>3</sup> and especially by King,<sup>4</sup> by Chamber-

<sup>1</sup> Stock and Blix, *Ber.*, **34**, 3039 (1901); Stock and Holle, *Ber.*, **41**, 2095 (1908).  
<sup>2</sup> Schneider, *J. prakt. Chem.*, [2] **32**, 206 (1885).

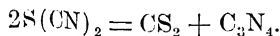
<sup>3</sup> Franklin, *J. Am. Chem. Soc.*, **46**, 507 (1922).

<sup>4</sup> R. I. King, Thesis, Stanford University, 1924.

lain<sup>5</sup> and by Hashimoto<sup>6</sup> have shown that mercuric thiocyanate, dry and free from admixture of basic salts, decomposes on heating in accordance with the equation,

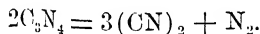


to form mercuric sulfide, carbon disulfide and carbonic anammonide. Koepfli<sup>7</sup> found that carbonic nitride contaminated with more or less sulfur is formed when cyanogen sulfide is heated,

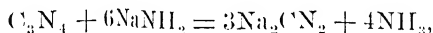


More recently<sup>8</sup> he has repeated Schneider's work on the decomposition of cyanogen trisulfide with the result that he was unable to obtain a product entirely free from sulfur. He concluded however that he had impure specimens of carbonic nitride in his hands.

Carbonic nitride is a yellow, extremely bulky, fluffy material which at temperatures approaching redness decomposes to form cyanogen and nitrogen,



It is undoubtedly highly polymerized and is soluble neither in water nor liquid ammonia. It absorbs moisture with extreme avidity when exposed to the atmosphere. Heated at 170° in a closed tube with aqueous hydrochloric acid it is hydrolyzed to cyanuric acid and ammonia, at higher temperatures completely to carbon dioxide and ammonia. It dissolves in fused sodium amide to form disodium cyanamide,



which is to say that carbonic anammonide reacts with the sodium ammonio base to form a sodium ammonocarbonate.

It appears that in so far as one may speak of a noncrystalline, infusible, insoluble product as possessing chemical individuality carbonic nitride is fairly certainly a definite chemical compound.

**Carbonous Anammonide,  $\text{C}_3\text{N}_2$ .** By heating tetraiodoimidazole Pauly and Waltzinger<sup>9</sup> obtained an insoluble, infusible, sepia-colored product of the composition represented by the formula,  $(\text{C}_3\text{N}_2)_x$ , which may be looked upon as a polymerized form of carbonous ni-

<sup>5</sup> P. I. Chamberlain, Thesis, Stanford University, 1931.

<sup>6</sup> T. Hashimoto, Jacques Loeb Laboratory, private communication.

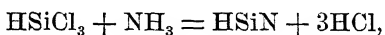
<sup>7</sup> J. B. Koepfli, Thesis, Stanford University, 1925.

<sup>8</sup> Private communication.

<sup>9</sup> Pauly and Waltzinger, *Ber.*, 46, 3129 (1913).

tride. However recent work by Wenzel<sup>10</sup> has shown that Pauly and Waltzinger's product is very probably a mixture of paracyanogen and carbon.

**Silicic Anammonide,  $(\text{Si}_3\text{N}_4)_x$ .** According to Weiss and Engelhardt<sup>13</sup> three nitrides of silicon of the formulas,  $\text{Si}_3\text{N}_4$ ,  $\text{SiN}$  and  $\text{Si}_2\text{N}_3$ , exist. The compounds represented by the first and second formulas may be regarded as respectively a silicic anammonide and as an anammonide of an ammono silico oxalic acid,  $\text{Si}_2\text{N}_2$ . The compound of the composition,  $\text{HSiN} \rightleftharpoons \text{HNSi}$ , obtained by the action of ammonia on silico chloroform,<sup>14</sup>



may be looked upon as either a silico formic anammonide or as ammono silicious acid.

Nitrides of the remaining elements of the fourth periodic group have been reported as follows, titanium nitrides,  $\text{Ti}_3\text{N}_4$ ,  $\text{TiN}$ ,  $\text{Ti}_5\text{N}_6$  and  $\text{TiN}_2$ , germanium nitrides,  $\text{Ge}_3\text{N}_4$  and  $\text{Ge}_5\text{N}_2$ ,<sup>15</sup> zirconium nitrides,  $\text{Zr}_3\text{N}_4$ ,  $\text{ZrN}$ ,  $\text{Zr}_2\text{N}_3$  and  $\text{Zr}_3\text{N}_5$ , and thorium nitride,  $\text{Th}_3\text{N}_4$ . Nitrides of tin and lead are not definitely known.

**Nitrides of the Elements of the Fifth Periodic Group.** Nitrogen may be said to separate from the diazo compounds as nitrous anammonide,  $\text{N}::\text{N} \rightarrow \text{N}_2$ . Phosphorus nitrides of the formulas,  $\text{P}_3\text{N}_5$  and  $\text{PN}$ , are to be regarded as phosphoric and phosphorous anammonides respectively, vanadium nitride,  $\text{VN}$ , as vanadous anammonide, arsenous nitride,  $\text{AsN}$ , as arsenous anammonide, antimony nitride,  $\text{SbN}$ , as antimonous anammonide and the tantalum nitrides,  $\text{Ta}_3\text{N}_5$  and  $\text{TaN}$  as tantalic anammonide and tantalous anammonides respectively. Bismuth nitride,  $\text{BiN}$ , is probably rather to be looked upon as a basic nitride than as an acid anammonide.

**Sulfuric Anammonide,  $\text{SN}_2$ , and Sulfurous Anammonide,  $\text{S}_2\text{N}_4$ .** These compounds are unknown. Attempts to prepare nitrides of sulfur of the composition represented by the above formulas or their ammonates by the action of nitridizing agents, in liquid ammonia, on hydrogen sulfide, on elementary sulfur and on tetrasulfur tetranitride have not been successful.<sup>16</sup>

**Tungstic Anammonide,  $\text{WN}_2$ .** Tungsten vapor combines with nitrogen to form a brown nitride of the composition represented by

<sup>10</sup> R. N. Wenzel, Thesis, Stanford University, 1927.

<sup>13</sup> Weiss and Engelhardt, *Z. anorg. Chem.*, **65**, 38 (1910); Blix and Wirbelauer, *Ber.*, **36**, 4227 (1903); Titherley, *J. Chem. Soc.*, **65**, 520 (1894).

<sup>14</sup> Ruff and Albert, *Ber.*, **38**, 2233 (1906).

<sup>15</sup> Schwarz and Denk, *Ber.*, **63**, 296 (1930); Johnson, *J. Am. Chem. Soc.*, **52**, 5160 (1930).

<sup>16</sup> Faw Yap Chuck, Thesis, Stanford University, 1926.

the above formula.<sup>17</sup> Under the action of water this compound yields ammonia and presumably  $\text{WO}_3$  or some hydration product thereof.

Rideal<sup>18</sup> obtained a black nitride of tungsten, to which he gave the formula,  $\text{W}_2\text{N}_3$ , by the action of ammonia on tungsten hexachloride. The compound may be a trivalent tungsten ammonotungstate,  $\text{WN.WN}_2$ .

Attempts to prepare an amide, imide or a nitride of tungsten by the action of potassium amide on tungsten halides using liquid ammonia as solvent were not successful.<sup>19</sup>

**Hypochlorous Anammonide,  $\text{N}:\text{Cl}_3$ .** Trichlorine nitride is related to the ammono hypochlorous acids as hypochlorous anhydride is to aquo hypochlorous acid. Nitrogen trichloride is therefore to be regarded an hypochlorous anammonide and not as the latter name would indicate a nitrous acid chloride.

According to Selewanow<sup>20</sup> trichlorine nitride is hydrolyzed by the action of water to aquo hypochlorous acid and ammonia while inversely it is formed by the action of ammonia on aquo hypochlorous acid. In view of the small difference in the negativity of chlorine and nitrogen as measured by Pauling<sup>21</sup> it is reasonable to suppose that  $\text{NCl}_3$  will be found acting sometimes as chlorine nitride,  $\text{N}:\text{Cl}_3$ , at other times as nitrogen trichloride,  $\text{N}:\text{Cl}_3$ . Attempts to prepare isomeric nitrogen chlorides were not successful.<sup>22</sup>

**Formic Anammonide,  $\text{HCN}$ .** Represented by the formula,  $\text{HN}::\text{C}$ , hydrocyanic acid is an ammono carbonous acid as has already been shown in some detail (*cf.* Chapter XII). The formula,  $\text{HC}::\text{N}$ , represents hydrocyanic acid as a formic anammonide.

**Acetic Anammonide,  $\text{CH}_3\text{CN}$ .** With the acid amidines established as the nitrogen analogs of the carboxylic acids (*cf.* Chapter XXI) it follows that the nitriles, which are related to the carbazyl acids as the acid anhydrides are related to the carboxylic acids, are to be regarded as acid anammonides.

The following well-known experimental facts support the view that acetonitrile is an acetic anammonide. It is formed by the dehydration of acetamide, which is an aquo-ammono acetic acid, and by the deammonation of acetamidine, an ammono acetic acid, just as the removal of water from aquo acetic acid yields acetic anhydride. In liquid ammonia solution it unites with potassium amide to form a potassium ammonoacetate after the manner of the

<sup>17</sup> Langmuir, *J. Am. Chem. Soc.*, **35**, 932 (1919); **37**, 1156 (1915).

<sup>18</sup> Rideal, *J. Chem. Soc.*, **55**, 44 (1889).

<sup>19</sup> Bergstrom, *J. Am. Chem. Soc.*, **47**, 2323 (1925).

<sup>20</sup> Selewanow, *Ber.*, **25**, 3618 (1892); **27**, 1012 (1894); Chapman and Vodden, *J. Chem. Soc.*, **95**, 143 (1909); W. A. Noyes, *J. Am. Chem. Soc.*, **42**, 2174 (1920).

<sup>21</sup> Pauling, *J. Am. Chem. Soc.*, **54**, 3577 (1932).

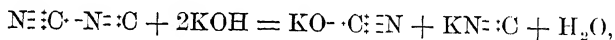
<sup>22</sup> W. A. Noyes, *J. Am. Chem. Soc.*, **47**, 2159 (1925).

formation of potassium aquoacetate by the action of potassium hydroxide on acetic anhydride. It reacts with water and the alcohols, hydrogen sulfide and the mercaptans, ammonia and the amines in a manner closely resembling the action of acetic anhydride on the same compounds. It follows from these considerations that the nitriles in general are to be looked upon as acid anammonides.

#### MIXED ANAMMONIDES

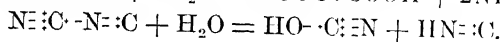
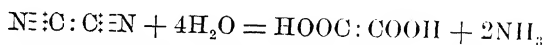
Just as certain compounds, such as acetyl nitrate or nitrosyl acetate,  $\text{CH}_3\text{CO-O-NO}_2$ , for example, are acid anhydrides containing residues of two acids so one might expect to find anammonides containing residues of two or even three different acids. Mixed anammonides of the former type are known but apparently none of the latter.

**Carbonic-Carbonous Anammonide**,  $\text{N}\equiv\text{C}\cdot\text{-N}\equiv\text{C}$ . Although experimental evidence in support of any surmise to the effect that cyanogen is a tautomeric compound is meager it nevertheless seems worth while to recall that the familiar formation of potassium cyanate and potassium cyanide by the action of potassium hydroxide on cyanogen may be plausibly explained on the assumption of the presence in cyanogen of a tautomeric form of the above formula. This formula represents a mixed carbonic-carbonous anammonide which, assuming the possibility of its existence, should react with potassium hydroxide in accordance with the equation,



to form equimolecular quantities of a potassium aquo-ammono-carbonate and potassium ammonocarbonite.

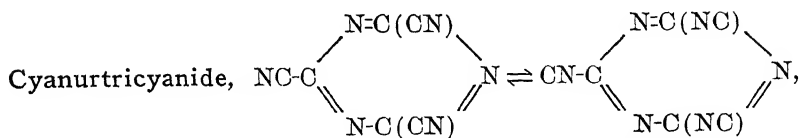
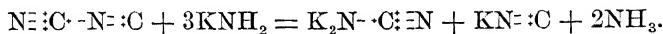
Furthermore the presence of ammonium oxalate, hydrocyanic acid, ammonium carbonate and urea among the products formed when a water solution of cyanogen is allowed to stand for a time is readily explained if it be assumed that the two tautomeric forms of cyanogen undergo hydrolysis simultaneously as represented by the equations,



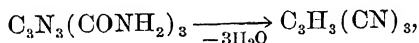
The cyanic acid primarily formed yields ammonium carbonate and urea.

Finally in a similar manner the formation of potassium ammono-carbonate and potassium ammonocarbonite by the interaction of

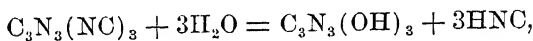
potassium amide and cyanogen in liquid ammonia solution may be explained as taking place as follows,<sup>22a</sup>



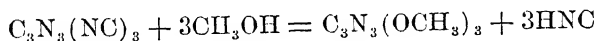
may be regarded as a trimer either of oxalic anammonide or of carbonic carbonous anammonide. Its formation by the dehydration of cyanuric acid triamide,



leads obviously to the structure represented by the first formula. On the other hand its hydrolysis to cyanuric acid and hydrocyanic acid,

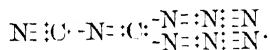


and its interaction with methyl alcohol to form trimethylcyanurate and hydrocyanic acid,<sup>22b</sup>

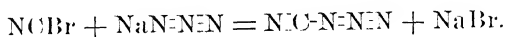


gives some support to the assumption that the constitution of cyanurtricyanide is as represented by the second formula.

Dicyandiazide, a Carbonic Nitric Anammonide,



By the action of cyanogen bromide on sodium azide Darzens<sup>23</sup> obtained a highly explosive product formed, as he believed, in accordance with the equation,



Such a compound would be a mixed anammonide of nitric acid and carbonic acid.

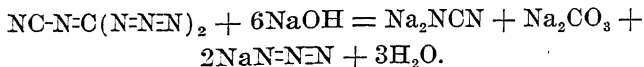
<sup>22a</sup> Cornell, *J. Am. Chem. Soc.*, **50**, 3311 (1928).

<sup>22b</sup> Ott, *Ber.*, **52**, 656 (1919).

<sup>23</sup> Darzens, *Compt. rend.*, **154**, 1232 (1912).

Recent investigations by Hart<sup>24</sup> have shown Darzens' compound to be a dimer of cyanazide and that as such it is to be represented by the formula given above and renamed dicyandiazide. Assuming hydrazoic acid to be an ammono nitric acid it follows that dicyandiazide, since it contains an ammono dicarbonic acid residue and two ammono nitric acid residues, is a mixed carbonic nitric anammonide.

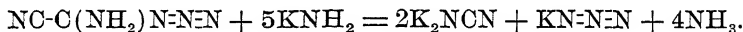
When a suspension of dicyandiazide in dilute sodium hydroxide is warmed for a short time disodium cyanamide, sodium aquocarbonate and sodium azide are formed practically quantitatively,



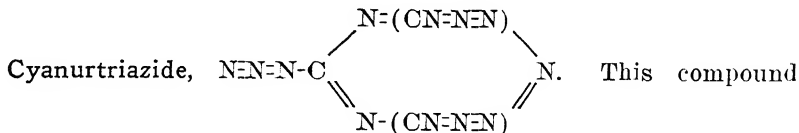
On treatment with an ether solution of ammonia dicyandiazide yields dicyanamidazide,



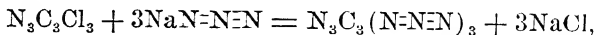
which in turn on warming in liquid ammonia solution with potassium amide is ammonolyzed to form dipotassium cyanamide and potassium azide,



That potassium cyanamide instead of the potassium salt of dicyandiamide was obtained Hart<sup>25</sup> explained on the basis of observations to the effect that dicyandiamide, which one might expect to obtain, is depolymerized to cyanamide when heated with potassium amide in liquid ammonia solution.



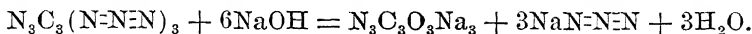
which is to be looked upon as a trimer of the unknown cyanazide of Darzens, is a cyclic carbonic nitric anammonide. It is formed by the action of sodium azide on cyanuric chloride,



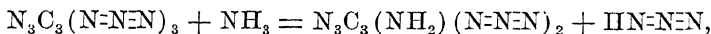
<sup>24</sup> Hart, *J. Am. Chem. Soc.*, **50**, 1922 (1928).

<sup>25</sup> An account of this work carried out with liquid ammonia as solvent was inadvertently omitted from Hart's published paper. (C. V. Hart, Thesis, Stanford University, 1927.)

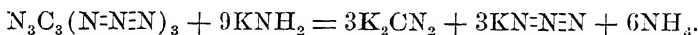
and when warmed with aqueous sodium hydroxide is hydrolyzed quantitatively to form sodium cyanurate and sodium azide.<sup>26</sup>



Hart showed that by the action of ammonia on cyanurtriazide in ether solution one of the azide groups is replaced by an amido group,



and that dipotassium cyanamide and potassium azide are formed when cyanurtriazide is warmed with potassium amide in liquid ammonia solution,



**Tetrasulfur Tetranitride,  $\text{S}_4\text{N}_4$ .** It has already been shown that this compound may be regarded as a mixed sulfurous thio sulfuric anammonide to which the formula,  $\text{N}::\text{S}::\text{N}::\text{S}::\text{N}::\text{S}::\text{N}$ , has been



given (cf. Chapter XVIII).

Selenium and tellurium form compounds with nitrogen of the respective empirical formulas  $\text{SeN}$  and  $\text{TeN}$ , which are very probably analogs of tetrasulfur tetranitride.

**Carbonous Hypochlorous Anammonide,  $\text{C}::\text{N}::\text{Cl}$ .** It is shown in another place (cf. Chapter XXIII) that cyanogen chloride reacts with water, ammonia, the alcohols and amines in a manner best explained on the assumption that it is a carbonic acid nitride-chloride. On the other hand its behavior toward certain readily oxidizable compounds leads quite as definitely to the conclusion that it is a derivative of hypochlorous acid.

Similar statements may be made concerning the behavior of the bromide and iodide of cyanogen. In so far therefore as the halogen cyanides may be represented by the formulas,  $\text{C}::\text{N}::\text{Cl}$ ,  $\text{C}::\text{N}::\text{Br}$  and  $\text{C}::\text{N}::\text{I}$ , they are respectively a carbonous hypochlorous anammonide, a carbonous hypobromous anammonide and a carbonous hypoiodous anammonide.

Hydriodic acid, hydrogen sulfide, sodium sulfite, sodium arsenite and sodium plumbite are augmented quantitatively to iodine, sulfur, sodium sulfate, sodium arsenate and lead peroxide respectively when treated with cyanogen iodide.<sup>27</sup> Cyanogen chloride and cyano-

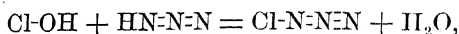
<sup>26</sup> Ott and Ohse, *Ber.*, **54**, 179 (1921); Taylor and Rinkenbach, *Bur. Mines Serial*, 2513 (1923).

<sup>27</sup> Chattaway and Wadmore, *J. Chem. Soc.*, **81**, 191 (1902); Gutmann, *Ber.*, **42**, 3623 (1909).

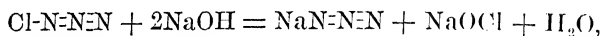


gen bromide augment these substances just as cyanogen iodide does excepting that, especially on the case of cyanogen chloride, the yield of augmentation products is much lower.

**Nitric Hypochlorous Anammonide, Chlorine Azide,  $\text{Cl}\cdot\text{N}::\text{N}::\text{N}$ .** This mixed anammonide, which is a highly explosive gas at ordinary temperatures, has been prepared by the action of sodium hypochlorite on sodium azide in dilute acetic acid solution.<sup>28</sup> Its formation in accordance with the equation,



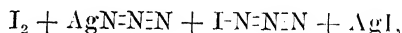
and its hydrolytic behavior toward sodium hydroxide solution as represented by the equation,



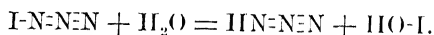
are in agreement with our assumption that it is an acid anammonide.

**Nitric Hypobromous Anammonide, Bromine Azide,  $\text{Br}\cdot\text{N}::\text{N}::\text{N}$ .** This compound has been obtained as a very volatile, orange-red liquid, freezing at  $-45^\circ$ , by passing bromine vapor diluted with nitrogen over dry sodium azide and condensing the product in a freezing mixture.<sup>29</sup> It is highly explosive and is hydrolyzed when in the vapor form it is passed into water.

**Nitric Hypoiodous Anammonide, Iodine Azide,  $\text{I}\cdot\text{N}::\text{N}::\text{N}$ .** That Hantzsch's triazidoiodide, prepared by the action of iodine in ether solution on silver azide,<sup>30</sup> is a mixed nitric hypoiodous anammonide is shown by the manner of its formation as represented by the equation,



and by Hantzsch's observations to the effect that it is hydrolyzed by the action of water to hydrazoic acid and aquo hypoiodous acid,



<sup>28</sup> Raschig, *Ber.*, **41**, 4194 (1908).

<sup>29</sup> Spencer, *J. Chem. Soc.*, **127**, 216 (1928).

<sup>30</sup> Hantzsch, *Ber.*, **33**, 522 (1900).

## CHAPTER XXII.

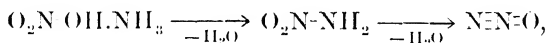
### ACID ANHYDRIDE-ANAMMONIDES.<sup>1</sup>

Some examples of compounds which are at the same time acid anhydrides and acid anammonides are listed herewith.

Carbon dioxide is a carbonic anhydride, carbonic nitride is a carbonic anammonide while a compound of the formula, NC-O-CN, would be a carbonic anhydride-anammonide. While cyanogen oxide is unknown it happens that the sulfur, selenium and tellurium compounds of the respective formulas, NC-S-CN, NC-Se-CN and NC-Te-CN, have been prepared.<sup>1a</sup>

In agreement with the view that cyanogen sulfide is the sulfur analog of the unknown compound, cyanogen oxide, are its ammoniation by the action of ammonia to a thio-ammono carbonic acid,  $\text{NC-S-CN} + 2\text{NH}_3 = \text{H}_2\text{N-C}(\text{NH})\text{S-C}(\text{NH})\text{NH}_2$ , its conversion to potassium cyanate and potassium thiocyanate under the action of potassium hydroxide,  $\text{NC-S-CN} + 2\text{KOH} = \text{KOCN} + \text{KSCN} + \text{H}_2\text{O}$ , and, as has been shown by unpublished work done in this laboratory, its decomposition by the action of heat to form carbon disulfide and carbonic nitride,  $2\text{NC-S-CN} = \text{CS}_2 + \text{C}_3\text{N}_4$ .

**Nitric Anhydride-Anammonide, Nitrous Oxide,  $\text{N}\equiv\text{N}::\text{O}$ .** Assuming that the nitric acid nitrogen and the ammonia nitrogen contained in ammonium nitrate persist as such after the salt has been converted into nitrous oxide and water by the action of heat it follows that as represented by the scheme,



nitrous oxide appears as a nitric anhydride-anammonide. It is reasonable to assume that nitric acid is first ammonolyzed to an aquo-ammono nitric acid (nitramide) which in turn immediately loses water to form a nitric anhydride-anammonide.<sup>2</sup> It is interesting to recall that Mendelejeff<sup>3</sup> explained the formation of nitrous oxide from ammonium nitrate in a manner practically identical with the above. The formation of nitrous oxide by the interaction of hydroxylamine and nitrous acid might lead one to conclude that it

<sup>1</sup> No attempt is made to classify these compounds.

<sup>1a</sup> Linnemann, *Ann. Chem.*, **120**, 36 (1861); Schneider, *J. prakt. Chem.*, [2] **32**, 187 (1896).

<sup>2</sup> Davis and Abrams, *J. Am. Chem. Soc.*, **47**, 1043 (1926).

<sup>3</sup> Mendelejeff, *Ber.*, **23**, 3469 (1890).

is a cyclic nitrous acid oxime. It has already been noted that it may be regarded as a hyponitrous acid anhydride (p. 191).

On the assumption that hydrazoic acid is an ammono nitric acid the formation of sodium azide by the action of nitrous oxide on sodium amide,  $\text{NaNH}_2 + \text{N}_2\text{O} = \text{NaN}=\text{N}=\text{N} + \text{H}_2\text{O}$ , is in harmony with the view that nitrous oxide is a nitric anhydride-anammonide.

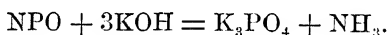
Preliminary experiments made some years ago in this laboratory and recently repeated under carefully controlled conditions,<sup>4</sup> have shown that small quantities of sodium nitrate and ammonia are formed, say in accordance with the equation,



when nitrous oxide is passed into fused sodium hydroxide. These observations lend support to the assumption that nitrous oxide is a nitric anhydride-anammonide.

On the other hand the decomposition of hyponitrous acid into nitrous oxide and water may be interpreted as showing that nitrous oxide is hyponitrous anhydride. Even though the chain formula for nitrous oxide has been fairly well established for nitrous oxide the possibility of its being a tautomeric compound is not thereby entirely excluded.

**Phosphoric Oxide-Nitride, Phosphoric Anhydride-Anammonide,  $\text{O}=\text{P}=\text{N}$ .** This compound is formed by the elimination of ammonia from the aquo-ammono phosphoric acids,  $\text{OP}(\text{NH}_2)_3$  and  $\text{OP}(\text{NH})\text{NH}_2$ , and is converted into potassium aquophosphate by the action of fused potassium hydroxide,



**Triacetamide, Acetic Anhydride-Anammonide,  $(\text{CH}_3\text{CO})_2\text{N}$ .** Triacetamide and tribenzamide are respectively an acetic anhydride-anammonide and a benzoic anhydride-anammonide.

Examples of mixed anhydride anammonides containing two different acid residues are the following.

**Carbazide,  $\text{OC}(\text{N}=\text{N})_2$ .** This compound, assuming the azide groups to be ammono nitric acid residues, is a carbonic anhydride-anammonide and at the same time a carbonic nitric anammonide.

**Benzoylisocyanate,  $\text{C}_6\text{H}_5\text{CO}-\text{N}=\text{CO}$ ,** a representative acyl isocyanate, is a mixed benzoic anhydride-anammonide carbonic anhydride-anammonide.

**Benzenesulfonylisocyanate,  $\text{C}_6\text{H}_5\text{SO}_2-\text{N}=\text{CO}$ ,** is a benzenesulfonic anhydride-anammonide and at the same time a carbonic anhydride-anammonide.

<sup>4</sup> Fernelius, Thesis, Stanford University, 1928.

*Diacetylcyanamide*,  $(\text{CH}_3\text{CO})_2\text{N}\cdot\text{CN}$ , is an acetic anhydride-anammonide acetic-carbonic anammonide.

*Benzoylazide*,  $\text{C}_6\text{H}_5\text{CO}\cdot\text{N}\cdot\text{N}\cdot\text{N}$ . This compound is a derivative of ammono nitric acid in the same sense that benzoyl nitrate,  $\text{C}_6\text{H}_5\text{CO}\cdot\text{O}\cdot\text{NO}_2$ , is a derivative of aquo nitric acid. Benzoyl nitrate is benzoic nitric anhydride. Benzoylazide is analogously at the same time a benzoic anhydride-anammonide and a benzoic nitric anammonide.

*Benzenesulfonazide*,  $\text{C}_6\text{H}_5\text{SO}_2\cdot\text{N}\cdot\text{N}\cdot\text{N}$ , is simultaneously a benzenesulfonic anhydride-anammonide and a benzenesulfonic nitric acid anammonide.

*Benzenesulfonyldichloramide*,  $\text{C}_6\text{H}_5\text{SO}_2\text{N}:\text{Cl}_2$ . This compound is formulated as a benzenesulfonic anhydride-anammonide hypochlorous anammonide.

# CHAPTER XXIII.

## ACID CHLORIDES.

In the middle column of Table 8 are given formulas for a number of nonmetallic chlorides. To the left, in column II will be found formulas for the partially hydrolyzed products of the respective acid chlorides. In column I are formulas for well known acids which in general may be obtained by the action of water on the respective chlorides and oxychlorides. In columns IV and V are given, in so far as they are known, the analogous compounds which might be expected to result from the ammonolytic action of ammonia on the chlorides formulated in column III.

TABLE 8.—Nonmetallic Chlorides.\*

I	II	III	IV	V
B(OH) <sub>3</sub>	.....	BCl <sub>3</sub>	.....	B(NH <sub>2</sub> ) <sub>3</sub>
[OC(OH) <sub>2</sub> ]	OCCl <sub>2</sub>	CCl <sub>4</sub>	N≡C Cl	N C NH <sub>2</sub>
.....	.....	.....	N <sub>3</sub> C <sub>3</sub> Cl <sub>3</sub>	N <sub>3</sub> C <sub>3</sub> (NH <sub>2</sub> ) <sub>3</sub>
.....	.....	.....	N <sub>3</sub> C <sub>3</sub> (Cl) <sub>2</sub> NH <sub>2</sub>	.....
.....	.....	.....	N <sub>3</sub> C <sub>3</sub> Cl(NH <sub>2</sub> ) <sub>2</sub>	.....
SiO <sub>2</sub> .xH <sub>2</sub> O	O(SiCl <sub>3</sub> ) <sub>2</sub>	Si Cl <sub>4</sub>	.....	Si(NH <sub>2</sub> ) <sub>4</sub>
.....	.....	.....	.....	HN Si(NH <sub>2</sub> ) <sub>2</sub>
.....	.....	.....	.....	N Si NH <sub>2</sub>
.....	.....	.....	.....	HN(SiN) <sub>2</sub>
TiO <sub>2</sub> .xH <sub>2</sub> O	HO TiCl <sub>3</sub>	Ti Cl <sub>4</sub>	N Ti Cl	Ti(NH <sub>2</sub> ) <sub>4</sub>
.....	.....	.....	.....	N Ti NH <sub>2</sub>
OSn(OH) <sub>2</sub>	OSnCl <sub>3</sub>	Sn Cl <sub>4</sub>	.....	[N Sn NH <sub>2</sub> ]
O <sub>2</sub> NOH	O <sub>2</sub> NCl	[NCl <sub>3</sub> ]	[HN N Cl]	[HN N NH <sub>2</sub> ]
OP(OH) <sub>3</sub>	OPCl <sub>3</sub>	PCl <sub>5</sub>	N P Cl <sub>2</sub>	N P(NH <sub>2</sub> ) <sub>2</sub>
.....	.....	.....	.....	N P NH <sub>2</sub>
P(OH) <sub>3</sub>	OPCl	PCl <sub>3</sub>	H <sub>2</sub> N P Cl <sub>2</sub>	HN P NH <sub>2</sub>
ClOH	.....	Cl-Cl	.....	Cl NH <sub>2</sub>
.....	.....	.....	.....	Cl <sub>2</sub> NH
C <sub>6</sub> H <sub>5</sub> COOH	C <sub>6</sub> H <sub>5</sub> COCl	C <sub>6</sub> H <sub>5</sub> COCl <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> C(NH <sub>2</sub> ) Cl <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> C(NH)NH <sub>2</sub>
.....	.....	.....	C <sub>6</sub> H <sub>5</sub> C(NH)Cl	.....

\* The bracketed formulas represent compounds known in the form of derivatives only.

In order to keep this chapter within reasonable bounds we have chosen to confine ourselves to a discussion of the action of ammonia and some of its derivatives on a limited number of acid chlorides, amide-chlorides, imide-chlorides and nitride-chlorides omitting all reactions involving the oxide-chlorides.

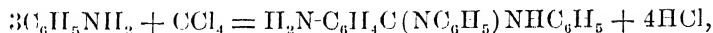
**Boron Trichloride,  $\text{BCl}_3$ .** According to Joannis<sup>1</sup> boron amide is formed when boron trichloride is treated with ammonia at  $-23^\circ$ ,  $\text{BCl}_3 + 3\text{NH}_3 = \text{B}(\text{NH}_2)_3 + 3\text{HCl}$ , and that the amide thus formed is readily deammonated when warmed, first to boron imide and thence at higher temperatures to boron nitride. Neither the amide-chloride,  $\text{B}(\text{NH}_2)\text{Cl}_2$ , nor the imide-chloride,  $\text{B}(\text{NH})\text{Cl}$ , is known.

**Carbon Tetrachloride.** Although carbon tetrachloride is very resistant to the action of hydrolyzing and ammonolyzing agents it none the less shows in an inconspicuous manner the properties of a carbonic acid chloride.

1. Good yields of guanidine have been obtained by heating carbon tetrachloride with ammonia under pressure at  $140^\circ$ .<sup>2</sup> In accordance with the equation,  $\text{CCl}_4 + 3\text{NH}_3 = \text{HNC}(\text{NH}_2)_2 + 4\text{HCl}$ , a carbonic acid chloride is ammonolyzed to an ammono carbonic acid.

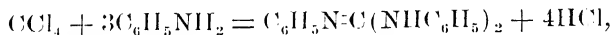
2. N-N'-Diphenyl-4-aminobenzamidine,<sup>3</sup> N-N'-N''-triphenylguanidine<sup>4</sup> and symmetrical diphenylurea<sup>5</sup> have been prepared by the interaction of carbon tetrachloride and aniline.

The formation of diphenylaminobenzamidine,



involves a Kolbe synthesis in that an ammono p-aminobenzoate is formed after the manner of the formation of p-hydroxybenzoic acid by the action of carbon tetrachloride on phenol in the presence of alkali.

The formation in small yield of N-N'-N''-triphenylguanidine by passing a mixture of carbon tetrachloride and aniline vapors over hot metals<sup>4</sup> may be represented by the equation,



and interpreted as involving the interaction of a carbonic acid chloride and aniline to form a triphenyl ammonocarbonate.

According to Hartung one of the products formed by the interaction of carbon tetrachloride and aniline is the carbonic acid

<sup>1</sup> Joannis, *Compt. rend.*, **138**, 1106 (1902); **139**, 346 (1904); Stock and Blix, *Ber.*, **34**, 3043 (1901); Stock and Holle, *Ber.*, **41**, 2095 (1905).

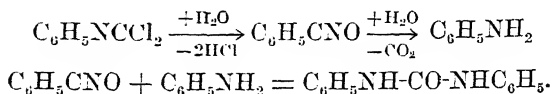
<sup>2</sup> Stähler, *Ber.*, **47**, 909 (1914).

<sup>3</sup> Weith, *Ber.*, **12**, 101 (1879).

<sup>4</sup> Löb, *Z. Elektrochem.*, **7**, 920 (1900-1901).

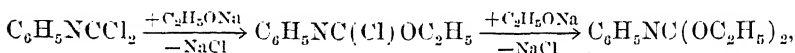
<sup>5</sup> Hartung, *J. Chem. Soc.*, **113**, 163 (1918).

aniline and hydrochloric acid. Phenylisocyanate, which is primarily formed, is hydrolyzed by the action of aqueous hydrochloric acid to aniline and carbon dioxide. Aniline is known to react with phenylisocyanate to form symmetrical diphenylurea. The reactions concerned may be summarized by means of the equations,

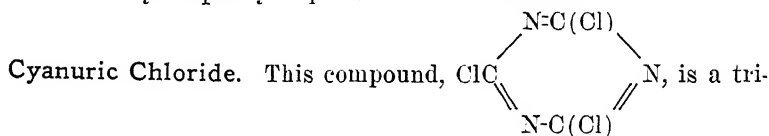


3. Phenylisocyanatedichloride reacts energetically with aniline to form *N-N'-N''*-triphenylguanidine, which is a triphenyl ammono-carbonate,  $\text{C}_6\text{H}_5\text{NCCl}_2 + 2\text{C}_6\text{H}_5\text{NH}_2 = \text{C}_6\text{H}_5\text{N}\cdot\text{C}(\text{NHC}_6\text{H}_5)_2 + 2\text{HCl}$ .

4. Phenylisocyanatedichloride is acted upon by one or two molecules of sodium ethylate as represented by the equation,

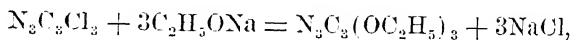


to form respectively an *O*-ethyl-*N*-phenyl carbonic acid chloride and an *O-O'*-diethyl-*N*-phenyl aquo-ammono-carbonate.<sup>14</sup>

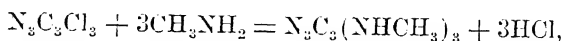


chloride of a cyclic tricarbonic acid. It is formed by the polymerization of cyanogen chloride and also by the action of phosphorus pentachloride on cyanuric acid.

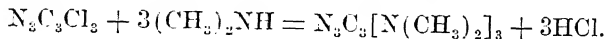
Cyanuric chloride is hydrolyzed by the action of water to cyanuric acid,  $\text{N}_3\text{C}_3\text{Cl}_3 + 3\text{H}_2\text{O} = \text{N}_3\text{C}_3(\text{OH})_3 + 3\text{HCl}$ , and is ammonolyzed by the action of ammonia to the cyclic ammono carbonic acid known as melamine,  $\text{N}_3\text{C}_3\text{Cl}_3 + 3\text{NH}_3 = \text{N}_3\text{C}_3(\text{NH}_2)_3 + 3\text{HCl}$ . It reacts with sodium ethylate to form triethylecyanurate,



with methylamine to form trimethylmelamine,



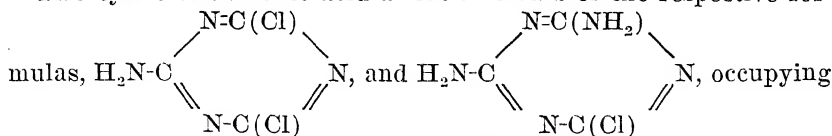
and with dimethylamine to form hexamethylmelamine,



<sup>14</sup> Lengfeld and Stieglitz, *Am. Chem. J.*, 16, 384 (1894); Hantzsch and Mai, *Ber.*, 28, 980 (1895).

The last two of these compounds are cyclic ammono carbonic acid esters formed by the action of ammono alcohols on a cyclic carbonic acid nitride-chloride.

Two cyclic tricarmonic acid amide-chlorides of the respective for-



positions between cyanuric acid chloride and melamine have been obtained by the action of ammonia on cyanuric acid chloride. It is interesting to observe that these compounds, in which the amide groups and the chlorine atoms are not attached to the same carbonic acid carbon atom, are stable as contrasted with the acid amide-chlorides and imide-chlorides discussed later.

**Silicon Tetrachloride**,  $\text{SiCl}_4$ , **Titanium Tetrachloride**,  $\text{TiCl}_4$ , **Stannic Chloride**,  $\text{SnCl}_4$ . The ammonolytic behavior of these acid chlorides has already been discussed. (*Cf.* Chapter XIII.)

**Nitrous Acid Chlorides.** Neither a nitrous acid amide-chloride,  $\text{H}_2\text{N}-\text{N}=\text{Cl}_2$ , nor an imide-chloride,  $\text{NH}=\text{N}-\text{Cl}$ , is known. Nitrogen trichloride (trichlorine nitride) is the anammonide of hypochlorous acid,  $\text{N}\equiv\text{Cl}_3$ , rather than a nitrous acid chloride,  $\text{N}\equiv\text{Cl}$ , though occasionally it enters into reactions which may reasonably be interpreted on the assumption that under some conditions it acts as a nitrous acid chloride. (*Cf.* Chapter XIV, p. 145.) It is interesting to compare this behavior of nitrogen trichloride in acting either as an hypochlorous anammonide or a nitrous acid chloride with monochloramine and nitrosyl chloride which apparently always act respectively as an ammono hypochlorous acid,  $\text{NH}_2-\text{Cl}$ , and a nitrous oxide-chloride,  $\text{O}=\text{N}-\text{Cl}$ , and never as containing, the one, hydrochloric acid chlorine, the other, hypochlorous acid chlorine.

**Phosphoric Nitride-Chloride**,  $\text{NPCl}_2$ . This analog of phosphoric oxide-chloride, unknown in the monomolecular state, has been prepared in no less than five polymeric forms.<sup>15</sup> The trimolecular compound is formed by the action of ammonia on phosphorus pentachloride,  $\text{PCl}_5 + \text{NH}_3 = \text{NPCl}_2 + 3\text{HCl}$ . Under the action of water it is hydrolyzed by way of certain mixed aquo-ammonio phosphoric acids finally to ortho phosphoric acid, ammonia and hydrochloric acid,  $\text{NPCl}_2 + 4\text{H}_2\text{O} = \text{OP}(\text{OH})_3 + \text{NH}_3 + 2\text{HCl}$ . By the action of liquid ammonia it is ammonolyzed to an ammonio phosphoric acid,  $\text{NPCl}_2 + 2\text{NH}_3 = \text{NP}(\text{NH}_2)_2 + 2\text{HCl}$ .<sup>16</sup> It has been observed to react with phenol and with aniline in accordance

<sup>15</sup> Stokes, *Am. Chem. J.*, **17**, 275 (1895); **19**, 782 (1897); Schenck and Römer, *Ber.*, **57**, 1343 (1924).

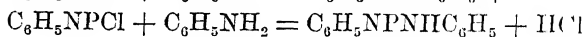
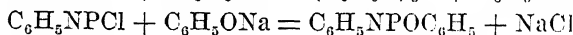
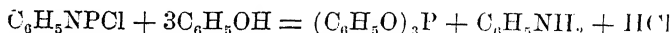
<sup>16</sup> Besson and Rosset, *Compt. rend.*, **145**, 1149 (1908).



with the equations,  $\text{NPCl}_2 + 2\text{C}_6\text{H}_5\text{OH} = \text{NP}(\text{OC}_6\text{H}_5)_2 + 2\text{HCl}$  and  $\text{NPCl}_2 + 2\text{C}_6\text{H}_5\text{NH}_2 = \text{NP}(\text{NHC}_6\text{H}_5)_2 + 2\text{HCl}$ <sup>17</sup> forming in the first case an O-O'-diphenyl ester of an aquo-ammonio phosphoric acid and the other an N-N'-diphenyl ester of an ammonio phosphoric acid.

**Phosphorous Amide-Chloride,  $\text{H}_2\text{NPCl}_2$ , and Phosphorous Imide-Chloride,  $\text{HNPCl}$ .** While neither the amide-chloride nor the imide-chloride is known in the free state it happens that a number of esters of each has been prepared, for example, compounds represented by the formulas,  $\text{C}_2\text{H}_5\text{HNPCl}_2$ ,  $(\text{C}_2\text{H}_5)_2\text{NPCl}_2$ ,  $(\text{CH}_3)_3(\text{C}_6\text{H}_5)\text{NPCl}_2$  and  $\text{C}_6\text{H}_5\text{NPCl}$ .<sup>17a</sup> These mixed ester-chlorides are formed by the action of the amines on phosphorus trichloride and are hydrolyzed by the action of water to aquo phosphorous acid, hydrochloric acid and the respective amines.

The phosphorous acid ester-chloride,  $\text{C}_6\text{H}_5\text{N}=\text{P}=\text{Cl}$ , called phosphazobenzenechloride by Michaelis and Schroeter, has been observed to act as an acid chloride with phenol, with sodium phenolate and with aniline as represented by the equations,



to form respectively a triphenyl aquophosphite, an O-N-diphenyl aquo-ammonio-phosphite and an N-N'-diphenyl ammoniophosphite. Phosphazobenzenechloride and the latter two esters are known in their dimeric forms.

*Chlorine* may be regarded, potentially at any rate, as a hypochlorous acid chloride,  $\text{Cl} \cdot \text{Cl}$ . It reacts with potassium hydroxide to form potassium chloride and potassium hypochlorite, and is partially hydrolyzed by the action of water into hypochlorous acid and hydrochloric acid,  $\text{Cl}_2 + \text{H}_2\text{O} = \text{HO} \cdot \text{Cl} + \text{HCl}$ .<sup>17b</sup>

**Carbylic Acid Chlorides, *Chloroform*,  $\text{HCCL}_3$ .** Although the acid chloride properties of chloroform are inconspicuous it is none the less true that its behavior toward water, alcohol, ammonia and aniline is distinctly that of a formic acid chloride.

At laboratory temperature it reacts with alcoholic sodium hydroxide to form triethyl orthoformate which is to say that an ethyl aquoformate is formed by the interaction of a formic acid chloride and sodium ethylate,  $\text{HCCL}_3 + 3\text{C}_2\text{H}_5\text{ONa} = \text{HC}(\text{OC}_2\text{H}_5)_3 + 3\text{HCl}$

Chloroform reacts with aqueous potassium hydroxide to form

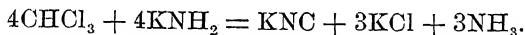
<sup>17</sup> Hofmann, *Ber.*, 17, 1909 (1884); Schenck and Römer, *Ber.*, 57, 1343 (1924).

<sup>17a</sup> Michaelis and Schroeter, *Ber.*, 27, 491 (1894); Michaelis, *Ann. Chem.*, 150, 220 (1908); Michaelis and Luxembourg, *Ber.*, 29, 711 (1896).

<sup>17b</sup> Richardson, *J. Chem. Soc.*, 33, 380 (1903); Jakowin, *Z. physik. Chem.*, 613 (1899); Bray, *J. Am. Chem. Soc.*, 32, 932 (1910).

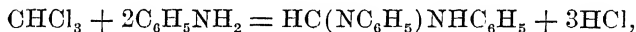
tassium formate, carbon monoxide and potassium chloride and with sodium amide to form sodium cyanide, sodium chloride and ammonia. In the one case the formic acid chloride is hydrolyzed to aquo formic acid,  $\text{HCCl}_3 + 3\text{H}_2\text{O} = \text{HCOOH} + 3\text{HCl}$ ,<sup>17c</sup> in the other it is ammonolyzed to hydrocyanic acid which is to be looked upon either as formic anammonide or as an ammono carbonous acid,  $\text{HCCl}_3 + 3\text{NH}_3 = \text{HCN} \rightleftharpoons \text{HNC} + 3\text{HCl}$ .

According to Kraus<sup>18</sup> potassium amide in liquid ammonia solution acts on chloroform to form potassium cyanide, potassium chloride and ammonia,

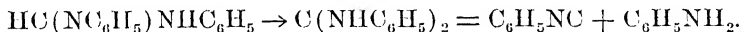


When chloroform is heated with aniline in a closed tube N-N'-diphenylformamidine is formed, and when warmed with aniline and alcoholic potassium hydroxide diphenylformamidine and phenylisocyanide are formed. By the interaction of chloroform, aniline and sodium amide in the presence of benzene phenylisocyanide is obtained.

The formation of diphenylformamidine takes place as represented by the equation,



in accordance with which a diphenyl ammonoformate is formed by the action of a formic acid chloride on aniline. Weith<sup>19</sup> having observed that diphenylformamidine at its boiling point decomposes slowly into phenylisocyanide and aniline it is reasonable to assume that diphenylformamidine is a tautomeric compound, which, acting as a diphenyl ammonocarbonite, loses aniline to form phenyl ammonocarbonite,



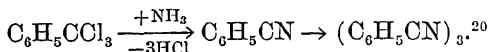
*1-1-1-Trichlorethane*,  $\text{CH}_3\text{CCl}_3$ , *1-1-1-Trichloropropane*,  $\text{CH}_3\text{CH}_2\text{CCl}_3$ , *1-1-1-Trichlor-2-methylpropane*,  $(\text{CH}_3)_2\text{CH}_2\text{CCl}_3$ , and *Hexachlorethane*,  $\text{CCl}_3\text{CCl}_3$ . In a sluggish manner these compounds, in their behavior toward potassium hydroxide, show the properties respectively of an acetic acid chloride, a propionic acid chloride, an isobutyric acid chloride and an oxalic acid chloride. Nothing is known of their behavior toward ammonia or potassium amide.

<sup>17c</sup> The carbon monoxide formed at the same time may be said to be the anhydride of an hypothetical carbonous acid.

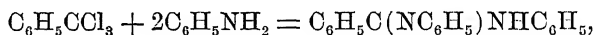
<sup>18</sup> Private communication.

<sup>19</sup> Weith, *Ber.*, **9**, 456 (1876).

Benzotrichloride,  $C_6H_5CCl_3$ . This benzoic acid chloride is hydrolyzed by the action of water to aquo benzoic acid and hydrochloric acid. It is simultaneously hydrolyzed and ammonolyzed by the action of aqua ammonia to aquo benzoic acid, aquo-ammono benzoic acid (benzamide) and benzoic anammonide (benzonitrile). Liquid ammonia ammonolyzes it quantitatively to a mixture of monomolecular and trimolecular benzonitrile,



It reacts with aniline,



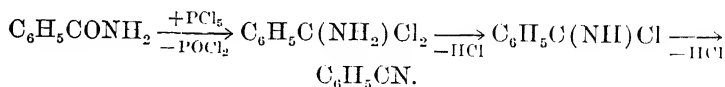
to form a diphenyl ammonobenzoate. Whether or not a hexa-alkyl or a hexa-aryl ammonobenzoate,  $C_6H_5C(NR_2)_3$ , may be obtained by the action of secondary amines on the acid chloride is unknown.

**Carbylic Acid Amide-Chlorides,  $RC(NH_2)Cl_2$ , and Imide-Chlorides,  $RC(NH)Cl$ .** These compounds, which in general decompose with the greatest ease into nitriles and hydrochloric acid, are formed by the action of hydrochloric acid on the nitriles and are to be looked upon as acid chlorides though they are not, accurately speaking, nitrogen analogs of the familiar carboxylic acid chlorides. They are more closely related to the unknown hydroxide-chlorides,  $RC(OH)Cl_2$  and  $RC(OH)_2Cl$ .<sup>21</sup>

**Formic Acid Imide-Chloride,  $HC(NH)Cl$ , Hydrocyanic Acid Sesquichloride,  $HN-CH-NH-CHCl_2 \cdot HCl$ , and Propionic Acid Imide-Chloride,  $C_2H_5C(NH)Cl$ .**<sup>22</sup>

It will suffice present purposes to say of these compounds that they show the properties of acid chlorides.

**Benzoic Acid Amide-Chloride,  $C_6H_5C(NH_2)Cl_2$ , and Benzoic Acid Imide-Chloride,  $C_6H_5C(NH)Cl$ .** According to Wallach<sup>23</sup> these two compounds are formed as intermediate products when benzamide, under the action of phosphorus pentachloride, is converted into benzonitrile,



<sup>20</sup> Niemann, Thesis, Stanford University, 1925.

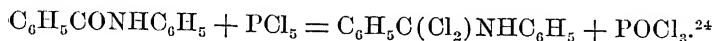
<sup>21</sup> Chlorhydrines of certain inorganic acids are known. For example, chloro sulfuric acid,  $ClSO_2OH$ , is at the same time an aquo sulfuric acid and a sulfuric acid chloride. The compound,  $ClCrO_2OK$ , is simultaneously a potassium salt and a chloride of chromic acid.

<sup>22</sup> Gattermann and Schnitzspahn, *Ber.*, 31, 1770 (1899); Michael and Wing, *Am. Chem. J.*, 7, 72 (1885-1886).

<sup>23</sup> Wallach, *Ann. Chem.*, 184, 19 (1877).

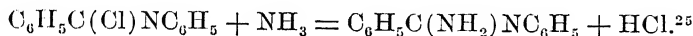
Both acid chlorides are very unstable, the first indeed has apparently never been isolated.

By the action of phosphorus pentachloride on benzanilide a phenyl derivative of benzoic acid amide-chloride is formed as represented by the equation,

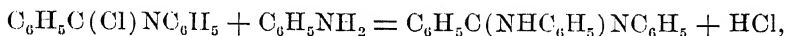


This compound readily loses hydrochloric acid thereby passing over into the ester-chloride,  $\text{C}_6\text{H}_5\text{C}(\text{Cl})=\text{NC}_6\text{H}_5$ , which containing no labile hydrogen, is a stable compound.

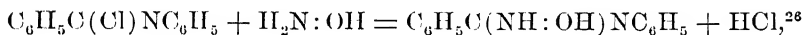
Many observations are on record which show the acid chloride properties of phenylbenzimidochloride. It is ammonolyzed by the action of aqua ammonia to phenylbenzamidine,



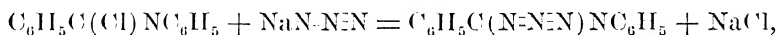
It reacts with aniline to form an N-N'-diphenyl ammonobenzoate,



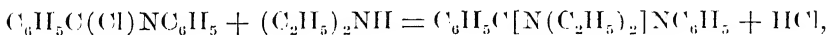
and with hydroxylamine to form benzanilide oxime,



a compound which is at the same time a benzoic acid oxime and a phenyl ammonobenzoate. It reacts with sodium azide,



to form a benzoic acid ester-azide which isomerizes immediately to 1-5 diphenyltetrazole,<sup>27</sup> and with diethylamine,



to form a diethyl phenyl ammonobenzoate.

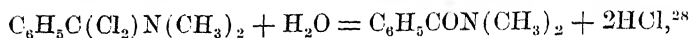
Benzoic acid ester-chlorides of the formula,  $\text{C}_6\text{H}_5\text{C}(\text{Cl}_2)\text{NR}_2$ , are stable compounds which show conspicuously the properties of acid chlorides. For example, N-N-dimethylbenzamidine chloride reacts energetically with water to yield dimethylbenzamide,

<sup>24</sup> Wallach and Hoffmann, *Ann. Chem.*, **184**, 79 (1877).

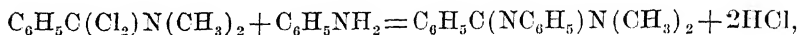
<sup>25</sup> v. Pechmann, *Ber.*, **30**, 1782 (1897).

<sup>26</sup> Ley, *Ber.*, **31**, 240 (1898).

<sup>27</sup> Schroeter, *Ber.*, **42**, 3360 (1909).



and with aniline in accordance with the equation,



to form N-N-dimethyl-N'-phenylbenzamidine<sup>29</sup> which is a dimethyl phenyl ester of an ammono benzoic acid.

<sup>28</sup> Hallmann, *Ber.*, 9, 846 (1876).

<sup>29</sup> v. Braun, *Ber.*, 37, 2680 (1904).

## CHAPTER XXIV.

### HYDROGEN PEROXIDE, HYDRAZINE AND HYDROXYLAMINE.

The attention of chemists has from time to time been called to certain striking resemblances shown by hydrogen peroxide, hydrazine and hydroxylamine in respect to their physical and chemical properties.<sup>1</sup>

Hydrazine is formally a nitrogen analog of hydrogen peroxide and as such may be looked upon, so to speak, as a hydrogen peroxide of the nitrogen system while hydroxylamine is a similar compound derived simultaneously from water and ammonia.

**Some Properties of Hydrogen Peroxide, Hydrazine and Hydroxylamine.** Hydrogen peroxide and hydrazine are liquids at ordinary temperatures. Hydroxylamine melts at 33°. All three compounds show to a conspicuous degree the phenomenon of superfusion. Sodium chloride, sodium nitrate and cane sugar have been found to be abundantly soluble in hydrogen peroxide,<sup>2</sup> hydrazine dissolves many salts, forming solutions which are conductors of electricity,<sup>3</sup> and fused hydroxylamine is a good solvent for salts.<sup>4</sup> All three compounds are miscible with water. Hydrazine and hydroxylamine absorb ammonia gas with considerable avidity and are abundantly soluble in liquid ammonia. The solubility of hydrogen peroxide in liquid ammonia has not been investigated. However the ready solubility of ammonia gas in hydrogen peroxide suggests the probability that liquid ammonia and hydrogen peroxide will be found to be miscible. A hydrogen peroxide hydrate,  $\text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ , and two hydrates of hydrazine,  $\text{H}_2\text{N} : \text{NH}_2 \cdot \text{H}_2\text{O}$  and  $\text{H}_2\text{N} : \text{NH}_2 \cdot 2\text{H}_2\text{O}$ , are known.<sup>4a</sup> No hydrate of hydroxylamine appears to be on record. Of the three compounds hydrogen peroxide only is known to form a compound with ammonia. According to Friedrichs,<sup>5</sup> hydrazine does not form an ammonate. Hydrogen peroxide and hydroxylamine are explosive. Hydrazine decomposes quietly at tempera-

<sup>1</sup> E. Wagner, *Chem. Zentr.*, 1899, I, 244; Angeli, *Atti. accad. lincci*, [5] 19, 94 (1910); Stieglitz and Senior, *J. Am. Chem. Soc.*, 38, 2727 (1906).

<sup>2</sup> Maas and Hatcher, *J. Am. Chem. Soc.*, 44, 2472 (1922).

<sup>3</sup> Welsh and Broderson, *J. Am. Chem. Soc.*, 37, 816 (1915).

<sup>4</sup> Lobry de Bruyn, *Rec. trav. chim.*, 11, 40 (1911).

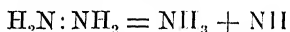
<sup>4a</sup> The formula for hydrazine,  $\text{H}_2\text{N} : \text{NH}_2$  has been adopted for use in this monograph. (See Chapter IV.)

<sup>5</sup> Friedrichs, *Z. anorg. Chem.*, 127, 221 (1923).

tures around 350°. All three compounds form metallic derivatives and unite with salts as solvates of crystallization. Many hydrazine and hydroxylamine derivatives of the alcohols, aldehydes, ketones and carbylic acids are known. Relatively few analogous derivatives of hydrogen peroxide have been prepared.

**Decomposition of Hydrogen Peroxide, Hydrazine and Hydroxylamine.** All three compounds in water solution in the presence of platinum black and other catalyzing agents undergo rapid decomposition; the first to water and oxygen, the second to ammonia and nitrogen together with more or less hydrogen, the third to ammonia, water, nitrogen, nitrous oxide and, especially when decomposition takes place in the presence of alkalis, limited amounts of nitrous acid.<sup>6</sup>

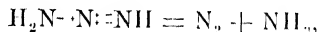
It is reasonable to speculate to the effect that the primary decomposition of these respective compounds takes place in accordance with the equations,



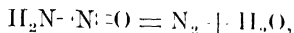
and that the imide groups appearing in the second and third equations interact with each other to form an ammono nitrous acid,



(cf. Chapter XIX) which in water solution undergoes hydrolysis to an aquo-ammono nitrous acid,  $\text{O}::\text{N}\cdot\text{NH}_2$ , or to aquo nitrous acid,  $\text{O}::\text{N}\cdot\text{OH}$ . The first of these hypothetical compounds would be expected to break down readily to nitrogen and ammonia,



the second to nitrogen and water,



the third is known to yield nitrogen and water when heated in aqueous ammonia solution.

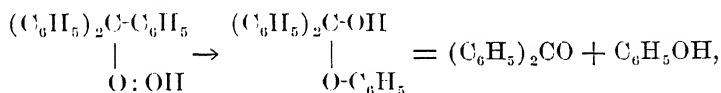
**Hydrogen Peroxide, Hydrazine and Hydroxylamine as Augmenting Agents.** All three compounds act both as augmenting and reducing agents; hydrogen peroxide conspicuously in both capacities, hydrazine and hydroxylamine generally as powerful reducing agents and only now and then as augmenters.

*Hydrogen Peroxide.* Some of the many reactions into which hy-

<sup>6</sup> Hofmann and Kroll, *Ber.*, 57, 937, 944 (1924).

hydrogen peroxide enters as an oxidizing agent or as a reducing agent or simultaneously in both capacities are as follows. It oxidizes ammonia to nitrous acid and thence to nitric acid, hydrogen sulfide to sulfur, sulfur dioxide and sulfuric acid, potassium cyanide to potassium cyanate. It reduces the free halogens, hypochlorites and other oxygenated halogen acids, the oxides of many of the heavy metals, Fehling's solution and the permanganates and chromates. In neutral or acid solution ferrous salts are oxidized; while suspended in alkaline solution ferric hydroxide is reduced to ferrous hydroxide. It precipitates lead dioxide from an alkaline solution of divalent lead. On the other hand, in its presence lead dioxide goes into solution in dilute nitric acid to form divalent lead nitrate. Suspended in alkaline solution manganous hydroxide is oxidized to manganese dioxide which inversely, in the presence of dilute acid and hydrogen peroxide, goes into solution as a manganous salt. Under the action of hydrogen peroxide yellow phosphorus is simultaneously oxidized to phosphorous and phosphoric acids and reduced to phosphine.

Hydrogen peroxide oxygen acts as an oxidizing agent when triphenylmethylhydroperoxide undergoes a Beckmann-like rearrangement to form benzophenone and phenol.<sup>7</sup> The rearrangement takes place in accordance with the scheme,



in accordance with which a tertiary alcohol group undergoes augmentation to a ketone group while at the same time hydrogen peroxide oxygen is reduced to water oxygen.

*Hydrazine.* Like hydrogen peroxide hydrazine acts both as an augmenting agent and a reducing agent, surpassing hydrogen peroxide in the latter capacity and lagging far behind in respect to the former. Only a comparatively few examples of the action of hydrazine and its derivatives as augmenting agents have been observed among which are the following.

Oxalic acid is formed, as represented by the equation,



when a water solution containing glyoxylic acid and hydrazine together with a small amount of sulfuric acid is boiled for a time. The aldehyde group is augmented to a carboxyl group while hydrazine is reduced to ammonia. Under similar conditions a solution containing formaldehyde and hydrazine yields carbon dioxide and

<sup>7</sup> Wieland and Maier, *Ber.*, 64, 1205 (1931); Franklin, *Chem. Revs.* (1934).

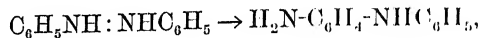


ammonia.<sup>8</sup> Formaldehyde is oxidized to carbonic acid and hydrazine is reduced to ammonia.

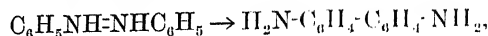
When hydrazine sulfate and sodium formate are heated together in the dry state or when the two salts in water solution are heated in a closed tube carbon dioxide and ammonia are formed,



The semidine rearrangement,

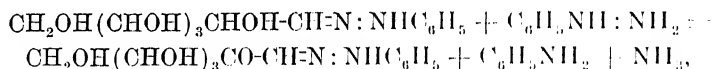


and the benzidine rearrangement,



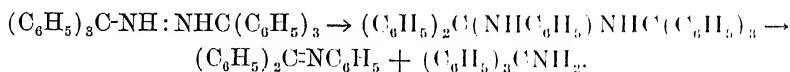
must be said to involve the augmenting action of hydrazine nitrogen.

Perhaps the most familiar examples of the action of hydrazines as augmenting agents are those concerned in the formation of osazones by the action of phenylhydrazine on the aldoses and ketoses. When glucose, for example, is converted into phenylglucosazone by the action of an excess of phenylhydrazine three successive reactions take place the second of which, represented by the equation,



involves the augmentation of a secondary alcohol group to a ketone group and the simultaneous reduction of phenylhydrazine to aniline and ammonia.

When symmetrical bis-triphenylmethylhydrazine is heated with zinc chloride benzophenonephenylimine and triphenylmethylaniline are formed.<sup>9a</sup>



One of the tertiary alcohol groups in bis-triphenylmethylhydrazine is augmented to a ketone group, hydrazine nitrogen at the same time undergoing reduction to ammonia nitrogen. The ketone acetal formed decomposes to yield the ketone-alcohol and a tertiary ammono alcohol.

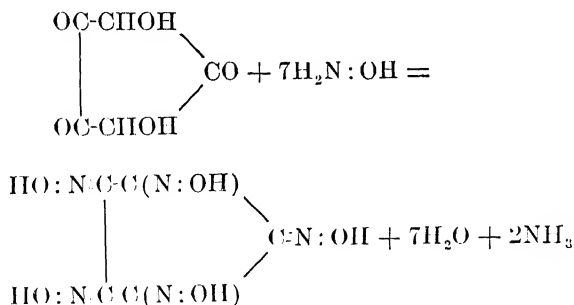
<sup>8</sup> Curtius, Darapsky and Müller, *Ber.*, **39**, 3413 (1916).

<sup>9</sup> Unpublished observations.

<sup>9a</sup> Stieglitz and Brown, *J. Am. Chem. Soc.*, **44**, 1274 (1922).

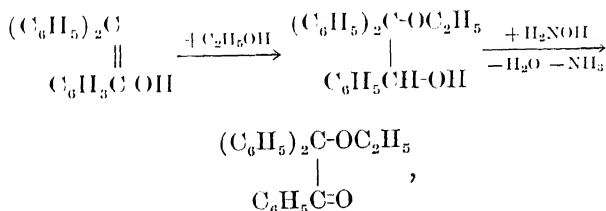
*Hydroxylamine.* Like hydrogen peroxide and hydrazine hydroxylamine acts both as an augmenting agent and as a reducing agent. It is not necessary here to consider examples of the long list of reactions into which hydroxylamine enters as a reducing agent. In this respect it follows, in a general way, the behavior of hydrogen peroxide and hydrazine. One is tempted to generalize to the effect that it excels hydrogen peroxide but does not equal hydrazine as a reducing agent and that it stands between these two compounds in respect to its efficacy as an augmenting agent. Since however hydroxylamine is not usually thought of as an augmenting agent it becomes desirable to recall some of the cases in which it so acts.

According to Biltz<sup>10</sup> the earliest observations on the augmenting action of hydroxylamine are due to E. von Meyer<sup>11</sup> who said that hydroxylamine acts essentially as an oxidizing agent in converting anthranol, C<sub>14</sub>H<sub>10</sub>O, into anthraquinone, C<sub>14</sub>H<sub>8</sub>O<sub>2</sub>, and to Nietzki and Benckiser,<sup>12</sup> who found that a pentoxime of leuconic acid is formed by the action of hydroxylamine on croconic acid. Two of the seven molecules of hydroxylamine entering into the reaction as represented by the equation,



bring about the dehydrogenation of the two secondary alcohol carbon atoms to ketone carbon atoms.

Biltz showed that the reactions represented by the scheme,



<sup>10</sup> Biltz, *Ber.*, **29**, 2080 (1896).

<sup>11</sup> E. von Meyer, *J. prakt. Chem.*, [2] **29**, 497 (1884).

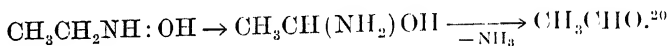
<sup>12</sup> Nietzki and Benckiser, *Ber.*, **19**, 303 (1886).

take place when an alcoholic solution of triphenylvinyl alcohol and hydroxylamine hydrochloride is heated and said that the part taken by the hydroxylamine is that of an oxidizing agent.

Piccini<sup>13</sup> has shown that by the action of hydroxylamine the sesquioxides of vanadium, titanium and molybdenum are oxidized to the respective dioxides, Tanatar,<sup>14</sup> that sulfur dioxide in water solution is oxidized to sulfuric acid, Haber,<sup>15</sup> that ferrous hydroxide suspended in an alkaline solution is oxidized to ferric hydroxide, Kjellin,<sup>16</sup> that stannous tin in alkali solution is oxidized to stannic tin, Gutmann,<sup>17</sup> that sodium arsenite in sodium hydroxide solution is oxidized to sodium arsenate and Hofmann and Kroll<sup>18</sup> that hydriodic acid and metallic copper are oxidized by the action of aqueous hydroxylamine hydrochloride, the former to free iodine, the latter to cuprous copper which was isolated as cuprous chloride.

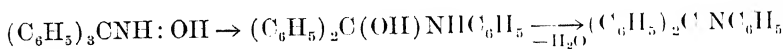
In a very interesting paper Hofmann, Hartmann and Kroll<sup>19</sup> have shown that hydroxylamine, hydrazine and their derivatives function as augmenting agents when by their action on aniline, the naphthylamines and other arylamines induline dyes are formed.

Further interesting examples of reactions in which hydroxylamine acts as an augmenting agent are the rearrangements of certain alkylhydroxylamines to form aldehydes. N-ethylhydroxylamine when heated with dilute hydrochloric acid yields acetaldehyde and ammonia,



Undergoing a Beckmann-like rearrangement N-ethylhydroxylamine yields aldehyde ammonia which breaks down to form acetaldehyde and ammonia.

In a similar manner when N-triphenylmethylhydroxylamine in ether solution is treated with phosphorus pentachloride benzophenonephenylimine is formed,



<sup>13</sup> Piccini, *Z. anorg. Chem.*, **11**, 111 (1896); *Gazz. chim. ital.*, **25**, 451, 452 (1897).

<sup>14</sup> Tanatar, *Z. anorg. Chem.*, **32**, 242 (1899).

<sup>15</sup> Haber, *J. prakt. Chem.*, [2] **79**, 172 (1909).

<sup>16</sup> Kjellin, *Chem. Zentr.*, **1922**, III, 340.

<sup>17</sup> Gutmann, *Ber.*, **55**, 3010 (1922).

<sup>18</sup> Hofmann and Kroll, *Ber.*, **57**, 944 (1924).

<sup>19</sup> Hofmann, Hartmann and Kroll, *Ber.*, **57**, 945 (1924).

<sup>20</sup> Kjellin, *Ber.*, **30**, 1895 (1897).

<sup>21</sup> Stieglitz and Leech, *J. Am. Chem. Soc.*, **36**, 289 (1914).

## CHAPTER XXV.

### AMMONO ALCOHOLS.

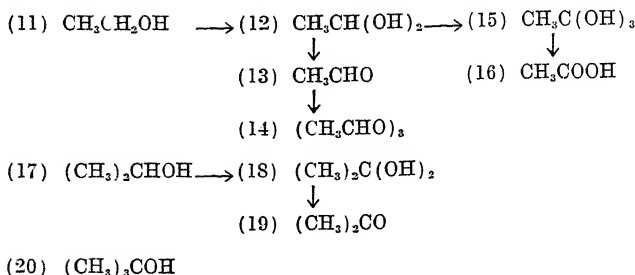
The established existence of a system of bases, acids and salts, in which nitrogen functions as the central element, just as oxygen is the element around which has been built up the familiar oxygen or Lavoisian system, leads directly to the question as to whether among the organic compounds of nitrogen one may find the analogs of such distinctive oxygen compounds as the ordinary alcohols, ethers, esters, aldehydes, ketones and carboxylic acids. The answer to this question is that such compounds are known in large numbers and that moreover their properties are such as to leave no doubt concerning the close analogies between the respective oxygen and nitrogen compounds.

The compounds which may be expected to show the properties of the alcohols, aldehydes, ketones and acids of a nitrogen or ammonia system may perhaps best be brought under review by giving first a table such as is frequently made use of for showing the relations between the alcohols and their oxidation products and then developing a similar table containing the alcohols of the nitrogen system and what may be analogously called their nitridation products. Following a brief explanatory discussion of the tables, we shall proceed to show in some detail that the formal relations thus indicated in the table are in harmony with experimental facts.

**Aquo Alcohols and Their Oxidation Products.** It is assumed that each oxidation step represented in Table 9 is brought about by the intrusion of an oxygen atom into a position between a carbon atom and a hydrogen atom and that the di-, tri-, and tetra-hydroxy compounds thus formed lose water to form the respective dehydration products indicated.

TABLE 9.—*Aquo Alcohols and Their Oxidation Products.*

Alcohols and Ethers		Aldehydes and Ketones		Carboxylic Acids		Carbonic Acids
(1) $\text{CH}_3\text{OH}$	$\longrightarrow$	(3) $\text{CH}_2(\text{OH})_2$	$\longrightarrow$	(6) $\text{HC}(\text{OH})_2$	$\longrightarrow$	(8) $\text{C}(\text{OH})_4$
		$\downarrow$		$\downarrow$		$\downarrow$
(2) $\text{CH}_3\text{OCH}_3$		(4) $\text{CH}_2\text{O}$		(7) $\text{HCOOH}$		(9) $\text{OC}(\text{OH})_2$
		$\downarrow$				$\downarrow$
		(5) $(\text{CH}_2\text{O})_3$				(10) $\text{CO}_2$



(1) *Methyl Alcohol*,  $\text{CH}_3\text{OH}$ , (2) *Dimethyl Ether*,  $\text{CH}_3\text{OCH}_3$ . In a real sense the alcohols and ethers are derivatives of water and as such it will be convenient from time to time to refer to them respectively as aquo alcohols and aquo ethers.

(3) *Methylene Glycol*,  $\text{CH}_2(\text{OH})_2$ , (4) *Methylene Oxide*,  $\text{CH}_2\text{O}$ . The molecule of methylene glycol may be looked upon as consisting of two molecules of water in each of which one atom of hydrogen is replaced by the divalent methylene group. As is well known, however, compounds containing two or more hydroxyl groups in combination with the same carbon atom are, in general, incapable of existence. Methylene glycol therefore loses water and passes over into formaldehyde. Alkyl, aryl and acyl derivatives of methylene glycol are stable compounds and are known as acetals. Methylene glycol is generally regarded as an alcohol rather than an acid.

(6) *Ortho Formic Acid*,  $\text{HC}(\text{OH})_2$ , is known only in the form of its esters. Reactions which might be expected to yield ortho formic acid give as a matter of fact ordinary aquo formic acid.

(8) *Ortho Carbonic Acid*,  $\text{C}(\text{OH})_4$ , represented as the final oxidation product of methyl alcohol, is unknown in the free state. Ortho carbonic acid exists in the form of esters, ordinary carbonic acid in the form of esters and salts.

(17) *Isopropyl Alcohol*,  $(\text{CH}_3)_2\text{CHOH}$ , is a representative secondary alcohol. On oxidation it may be assumed to be converted into isopropylidene glycol which immediately loses water to form acetone, a typical aquo ketone.

(20) *Trimethyl Carbinol*,  $(\text{CH}_3)_3\text{OH}$ , is a tertiary aquo alcohol.

**Ammono Alcohols and Their Nitridation Products.** With the relationships between the alcohols, ethers, aldehydes, acids and ketones of the oxygen system thus recapitulated we are prepared to follow in Table 10 a summary of the analogous compounds of the nitrogen system.

It is assumed that we have a nitridizing agent at our disposal wherewith to effect the nitridation reactions indicated and that the di-, tri- and tetra-amino compounds thus formed lose ammonia to give the respective deammonation products indicated.

TABLE 10.—Ammono Alcohols and Their Nitridation Products.

Alcohols and Ethers	Aldehydes and Ketones	Carbazylic Acids	Carbonic Acids
(1) $\text{CH}_3\text{NH}_2$	$\rightarrow$ (4) $\text{CH}_2(\text{NH}_2)_2$	$\rightarrow$ (8) $\text{HC}(\text{NH}_2)_3$	$\rightarrow$ (11) $\text{C}(\text{NH}_2)_4$
(2) $(\text{CH}_3)_2\text{NH}$	$\downarrow$ (5) $\text{CH}_2\text{=NH}$	$\downarrow$ (9) $\text{HC}(\text{NH})\text{NH}_2$	$\downarrow$ (12) $\text{HNC}(\text{NH}_2)_2$
(3) $(\text{CH}_3)_3\text{N}$	$\downarrow$ (6) $(\text{CH}_2)_3\text{N}_2$	$\downarrow$ (10) $\text{HCN}$	$\downarrow$ (13) $\text{H}_2\text{NCN}$
	$\downarrow$ (7) $(\text{CH}_2)_6\text{N}_4$		$\downarrow$ (14) $\text{HN}(\text{CN})_2$
			$\downarrow$ (15) $\text{C}_3\text{N}_4$
(16) $\text{CH}_3\text{CH}_2\text{NH}_2$	$\rightarrow$ (17) $\text{CH}_3\text{CH}(\text{NH}_2)_2$	$\rightarrow$ (20) $\text{CH}_3\text{C}(\text{NH}_2)_3$	
	$\downarrow$ (18) $\text{CH}_3\text{CH=NH}$	$\downarrow$ (21) $\text{CH}_3\text{C}(\text{NH})\text{NH}_2$	
	$\downarrow$ (19) $(\text{CH}_3\text{CH=NH})_3$	$\downarrow$ (22) $\text{CH}_3\text{CN}$	
(23) $(\text{CH}_3)_2\text{CHNH}_2$	$\rightarrow$ (24) $(\text{CH}_3)_2\text{C}(\text{NH}_2)_2$		
	$\downarrow$ (25) $(\text{CH}_3)_2\text{C=NH}$		
(26) $(\text{CH}_3)_3\text{CNH}_2$			

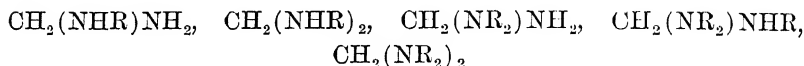
The formulas in the first column represent ammono alcohols and ethers, those in the second ammono aldehydes and related compounds, those in the third ortho ammono formic acid, ortho ammono acetic acid and their deammonation products and finally those in the fourth represent ortho ammono carbonic acid and its deammonation products.

(1) *Methylamine*,  $\text{CH}_3\text{NH}_2$ , is a nitrogen analog of methyl alcohol and as such is to be looked upon as an ammono methyl alcohol.

(2) *Dimethylamine*,  $(\text{CH}_3)_2\text{NH}$ , a dimethyl derivative of ammonia in which the nitrogen still remains in combination with a hydrogen atom, is also a primary ammono methyl alcohol. It may reasonably be called a diprimary ammono methyl alcohol.

(3) *Trimethylamine*,  $(\text{CH}_3)_3\text{N}$ , the ammonia analog of dimethyl ether is an ether of the nitrogen system.

(4) *Methylenediamine*,  $\text{CH}_2(\text{NH}_2)_2$ , like its oxygen analog methylene glycol, is unknown. Just as the latter is usually assumed to be an alcohol rather than an acid, so methylenediamine is an ammono alcohol or an ammono glycol, whose derivatives of the respective formulas,



in which R represents alkyl, aryl or acyl groups, are acetals of the nitrogen system.

(5) *Methyleneimine*,  $\text{CH}_2=\text{NH}$ , is a representative of a type of compounds impossible of existence among the derivatives of water. It is an aldehyde by virtue of the presence of a double bond between carbon and nitrogen, and, since it contains an imido group, it is at the same time either an alcohol or an extremely weak acid. We shall find it convenient to speak of the alkylideneimines,  $\text{RCH}=\text{NH}$ , as ammono aldehyde-alcohols and of their alkyl and aryl derivatives,  $\text{RCH}=\text{NR}$ , as ammono aldehyde-ethers. Compounds represented by the formulas,  $\text{RCH}=\text{N}(\text{OCR})$  and  $\text{RCH}=\text{N}(\text{NHCR})$ , are ammono aldehyde-esters. Methyleneimine itself has never been prepared.

(6) *Methylene Nitride*,  $\text{CH}_2\text{N}=\text{CH}_2$ , contains two ammono formaldehyde groups and is to be regarded as a diformaldehyde-acetal. Hydrobenzamide,  $(\text{C}_6\text{H}_5\text{CH})_3\text{N}_2$ , which is a triphenyl derivative of methylene nitride is a well-known compound.

(7) *Hexamethylenetetramine*,  $(\text{CH}_2)_6\text{N}_4$ , a dimer of the unknown methylene nitride is, as nearly as the trivalency of nitrogen permits, the nitrogen analog of trioxymethylene.

(8) *Ortho-Ammono Formic Acid*,  $\text{HC}(\text{NH}_2)_3$ , is the nitrogen analog of ortho-aquo formic acid and like the latter is unknown. Reactions which might be expected to yield it give instead the one or

the other of its deammonation products, namely, formamidine or hydrocyanic acid.

(9) *Formamidine*,  $\text{HC}(\text{NH})\text{NH}_2$ , is an ammono formic acid. Many alkyl and aryl derivatives of formamidine are known which are to be looked upon as esters of ammono formic acid.

(10) *Hydrocyanic Acid*. The formula,  $\text{HCN}$ , represents hydrocyanic acid as formic anammonide. Represented by the formula,  $\text{CNH}$ , it is an ammono carbonous acid.

(11) *Ortho Ammono Carbonic Acid*,  $\text{C}(\text{NH}_2)_4$ . This hypothetical compound and its deammonation products are the carbonic acids of the nitrogen system. (Cf. Chapter X.)

(16) *Ethylamine*,  $\text{C}_2\text{H}_5\text{NH}_2$ , and *Diethylamine*,  $(\text{C}_2\text{H}_5)_2\text{NH}$ , the nitrogen analogs of ordinary ethyl alcohol, are primary ammono alcohols. Triethylamine,  $(\text{C}_2\text{H}_5)_3\text{N}$ , is the nitrogen analog of ordinary diethyl ether.

(17) *Ethylidenediamine*,  $\text{CH}_3\text{CH}(\text{NH}_2)_2$ , is the immediate homolog of ammono methylene glycol and like the latter is known in the form of certain alkyl, aryl and acyl derivatives.

(18) *Ethylidencimine*,  $\text{CH}_3\text{CH}=\text{NH}$ . Like methyleneimine this compound is a mixed aldehyde-alcohol. It is known both in the monomolecular and trimolecular forms. Aldehyde-ethers represented by the formula  $\text{RCH}=\text{NR}$  are known as Schiff bases.

(19) *Ethylidene Nitride*, *Hydracetamide*,  $(\text{CH}_3\text{CH})_3\text{N}_2$ , formally an ammono acetaldehyde-acetal, though registered in Beilstein, is probably nonexistent.

(20) *Ortho-Ammono Acetic Acid*,  $\text{CH}_3\text{C}(\text{NH}_2)_3$ , is known neither in the free state nor in the form of esters.

(21) *Acetamidine*,  $\text{CH}_3\text{C}(\text{NH})\text{NH}_2$ , is the nitrogen analog of ordinary acetic acid and as such is an ammono acetic acid. Many esters and metallic salts of this and other carbazylie acids have been prepared.

(22) *Methyl Cyanide*,  $\text{CH}_3\text{CN}$ , which is related to acetamidine as acetic anhydride is related to aquo acetic acid, is acetic anammonide. The isomeric methyl isocyanide is an ammono carbonous acid ester.

(23) *Isopropylamine*,  $(\text{CH}_3)_2\text{CHNH}_2$ , and *Di-isopropylamine*,  $(\text{CH}_3)_2\text{CH}\cdot\text{NH}\cdot\text{CH}(\text{CH}_3)_2$ , are secondary ammono alcohols. Ethyl-isopropylamine,  $\text{CH}_3\text{CH}_2\text{NH}\cdot\text{CH}(\text{CH}_3)_2$ , is a mixed primary-secondary ammono alcohol.

(24) *Isopropylidenediamine*,  $(\text{CH}_3)_2\text{C}(\text{NH}_2)_2$ , like isopropylidene glycol, is unknown.

(25) *Isopropylidencimine*,  $(\text{CH}_3)_2\text{C}=\text{NH}$ , is formally a mixed ketone-alcohol. Though this particular compound is unknown a number of aromatic and mixed aliphatic-aromatic ketimines have been prepared.



(26) *Tertiary Butylamine*,  $(\text{CH}_3)_3\text{CNH}_2$ , and *Ditertiary Butylamine*,  $(\text{CH}_3)_3\text{C-NH-C}(\text{CH}_3)_3$ , are tertiary<sup>1</sup> ammono alcohols. Ethyl-tertiarybutylamine,  $\text{CH}_3\text{CH}_2\text{-NH-C}(\text{CH}_3)_3$ , is a mixed primary-tertiary alcohol. Isopropyltertiarybutylamine,  $(\text{CH}_3)_2\text{CH-NH-C}(\text{CH}_3)_3$ , is a secondary-tertiary ammono alcohol.

**The Alkylamines.** Having pointed out the formal relationship which the alkylamines bear to the alcohols and ethers we now proceed to determine the extent to which we are justified in regarding the alkylamines as alcohols and ethers of the nitrogen system of compounds. The nitrogen analogs of the aldehydes and carboxylic acids will be discussed in later chapters.

**The Alkylamines as Solvents.** As a solvent for salts, acids and bases water stands preeminent, while for the hydrocarbons and other nonpolar compounds in general its solvent power is poor to practically nil. Methyl alcohol on the other hand dissolves a comparatively limited number of salts and for such as are soluble its solvent power is much below that of water. Methyl alcohol is, however, an excellent solvent for compounds of carbon. Ether dissolves but few salts and those in general only sparingly while as a solvent for carbon compounds it surpasses methyl alcohol.

Similar relations with respect to their properties as solvents hold for ammonia and the amines. Ammonia is inferior to water as a general solvent for salts,<sup>2</sup> acids and bases but is much superior as a solvent for compounds of carbon. Such compounds, for example, as benzene and naphthalene are distinctly soluble, whilst aniline, and nitrobenzene are miscible, and many other organic compounds which are slightly soluble in water, dissolve abundantly in liquid ammonia.

As a solvent for salts methylamine is inferior to ammonia while it and other amines far surpass ammonia as solvents for compounds of carbon. Observations on the solubilities of inorganic and organic compounds in the alkylamines have been made by Gibbs, Fitzgerald, Elsey and by Bergstrom, Gilkey and Lund.<sup>3</sup>

**Solubility of the Alkylamines in Liquid Ammonia.** Another respect in which the alkylamines resemble the alcohols and ethers has to do with their solubility in liquid ammonia. It will be recalled that methyl alcohol, ethyl alcohol, the two propyl alcohols and tertiary butyl alcohol are miscible with water in all proportions while the respective ethers form two phase systems. An in-

<sup>1</sup> It is to be observed that the term tertiary as used in naming these butylamines has no connection whatever with the same word as here used for describing the same amines as alcohols.

<sup>2</sup> Excepting that certain salts, such as the iodides of silver, lead and mercury, are extremely soluble in liquid ammonia.

<sup>3</sup> Gibbs, *J. Am. Chem. Soc.*, **26**, 1395 (1906); Fitzgerald, *J. Phys. Chem.*, **16**, 621 (1912); Elsey, *J. Am. Chem. Soc.*, **42**, 2080 (1920); Bergstrom, Gilkey and Lund, *Ind. Eng. Chem.*, **24**, 57 (1932).

spection of Table 11 will show that a similar situation exists with respect to the solubility of the amines in liquid ammonia. Pairs of liquids which mix in all proportions are indicated in the table by m, those which form two phases by 2.<sup>4</sup>

TABLE 11.—*Solubilities of the Amines in Liquid Ammonia.*

Alcohols and Ethers in Water at	Alkylamines in Liquid Ammonia at				
	20°		20°	0°	—33°
Methyl alcohol .....	m	Methylamine .....	m	m	m
Dimethyl ether .....	2	Dimethylamine .....	m	m	m
Ethyl alcohol .....	m	Trimethylamine .....	m	m	m
		Ethylamine .....	m	m	m
		Diethylamine * .....	m	m	m
Diethyl ether .....	2	Triethylamine .....	m	2	2
n-Propyl alcohol .....	m	n-Propylamine .....	m	m	m
		n-Dipropylamine .....	m	2	2
n-Propyl ether .....	2	n-Tripropylamine .....	2	2	2
Isoamyl alcohol .....	2	Isoamylamine * .....	m	m	m
		Diisoamylamine .....	2	2	2
Isoamyl ether .....	2	Triisoamylamine .....	2	2	2
Hexyl alcohol .....	2	Hexylamine .....	m	..	2

\* Two liquid phases at —80°.

**The Boiling Points of Methylamine, Dimethylamine and Trimethylamine.** As a general rule the substitution of the methyl group for hydrogen in the hydrides of the elements of the fourth, fifth, sixth and seventh periodic groups yields compounds boiling at much higher temperatures than their respective parent compounds as will be seen by an inspection of Table 12. The methyl derivatives of hydrofluoric acid and water are conspicuous exceptions to this rule.

TABLE 12.—*Boiling Points.*

T		T		T		T	
CH <sub>4</sub>	—160°	NH <sub>3</sub>	—33°	H <sub>2</sub> O	100°	HF	19°
CH <sub>3</sub> CH <sub>3</sub>	—93	CH <sub>3</sub> NH <sub>2</sub>	—6.7	CH <sub>3</sub> OH	65	CH <sub>3</sub> F	—78
CH <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub>	—45	(CH <sub>3</sub> ) <sub>2</sub> NH	7.2	(CH <sub>3</sub> ) <sub>2</sub> O	—23		
CH(CH <sub>3</sub> ) <sub>3</sub>	—10	(CH <sub>3</sub> ) <sub>3</sub> N	3.5				
C(CH <sub>3</sub> ) <sub>4</sub>	+9.5						
		PH <sub>3</sub>	—85	H <sub>2</sub> S	—65	HCl	—85
		CH <sub>3</sub> PH <sub>2</sub>	—14	CH <sub>3</sub> SH	6	CH <sub>3</sub> Cl	—23
		(CH <sub>3</sub> ) <sub>2</sub> PH	25	(CH <sub>3</sub> ) <sub>2</sub> S	37		
		(CH <sub>3</sub> ) <sub>3</sub> P	41				

The boiling point of methyl fluoride is 97° below that of hydrofluoric acid and the boiling points of methyl alcohol and dimethyl ether are respectively 35° and 123° below the boiling point of water.

In view of the many close analogies between water and ammonia

<sup>4</sup> Unpublished observations.

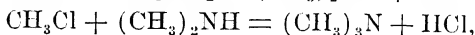
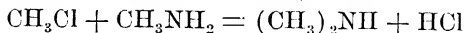
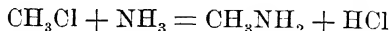
one might expect to find the boiling points of ammonia and its methyl derivatives falling successively from ammonia to trimethylamine. While this expectation is not in accord with the facts, it is none the less true that compared with the large rise in the boiling points brought about by the substitution of methyl groups in methane, phosphine, hydrogen sulfide and hydrochloric acid, the effects produced by the replacement of one and two hydrogen atoms in ammonia are relatively small while the boiling point of dimethylamine is actually depressed by the introduction of a third methyl group to form the ammono ether.

**The Electrical Conductivity of Solutions in the Alkylamines.** Investigations upon the electrical conductance of solutions of salts in the alkylamines<sup>5</sup> have shown that as the ionizing powers of water, methyl alcohol and dimethyl ether fall off in the order named so methylamine is a poorer ionizing agent than ammonia, dimethylamine poorer than methylamine while with trimethylamine ionizing power has practically disappeared.

**Amines of Crystallization.** Water unites with a large variety of salts as so-called water of crystallization. The alcohols much less frequently form analogous addition compounds while it is only occasionally that an ether unites with a salt as ether of crystallization.

Now entirely similar relations exist between ammonia and its alkyl derivatives in respect to the readiness with which they form addition compounds with salts. Ammonia itself quite equals or probably even exceeds water in its capacity to form addition compounds with salts. Methylamine unites with a large number of salts as methylamine of crystallization,<sup>6</sup> while only a few compounds containing dimethylamine and diethylamine of crystallization and a single one containing trimethylamine of crystallization are registered in Beilstein. It is interesting to note further that aniline and other aromatic amines, urea and other acid amides, form addition products with a considerable number of salts.

**Formation of the Amines.** 1. The reactions involved in the formation of methylamine, dimethylamine and trimethylamine by the interaction of methyl chloride and ammonia,



<sup>5</sup> Kahlenberg and Ruhoff, *J. Phys. Chem.*, 7, 254 (1903); Shinn, *J. Phys. Chem.*, 11, 557 (1907); Franklin and Gibbs, *J. Am. Chem. Soc.*, 29, 1389 (1907); Fitzgerald, *J. Phys. Chem.*, 16, 621 (1912); Elsey, *J. Am. Chem. Soc.*, 42, 2454 (1920).

<sup>6</sup> Bonnefoi, *Ann. chim. phys.*, [7] 23, 317 (1901); Elsey, *J. Am. Chem. Soc.*, 42, 2080 (1920).

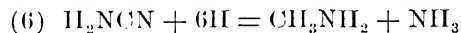
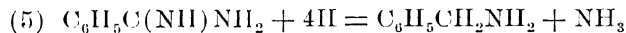
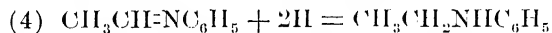
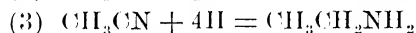
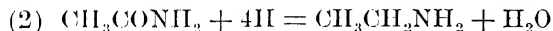
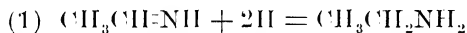
are identical in principle with those which take place when the hydrogen in water is replaced by ethyl groups to form ethyl alcohol and diethyl ether.

2. Methylamine is formed by the action of ammonia on methyl nitrate and on dimethyl sulfate. The two esters are ammonolyzed by the action of ammonia just as under the action of water they undergo hydrolytic decomposition.

3. Methyl iodide and sodium amide interact in the presence of liquid ammonia,  $\text{CH}_3\text{I} + \text{NaNH}_2 = \text{CH}_3\text{NH}_2 + \text{NaI}$ , to form methylamine. Under similar treatment ethyl iodide yields ethylamine and ethylene, n-propyl iodide yields n-propylamine and propylene, isobutyl chloride yields isobutylamine and isobutylene.<sup>7</sup> The behavior of alkyl halides toward sodium amide thus closely resembles their behavior toward sodium hydroxide.

4. Methyl alcohol has been ammonolyzed to methylamine by heating it with ammonium chloride or with ammonated zinc chloride,  $\text{CH}_3\text{OH} + \text{NH}_3 = \text{CH}_3\text{NH}_2 + \text{H}_2\text{O}$ . Ethylamine is obtained in small yield when ethyl alcohol and ammonium chloride are heated together at  $300^\circ$ .

5. Just as aquo alcohols are formed by the reduction of aquo aldehydes and carboxylic acids so ammono alcohols are obtained by the action of reducing agents on ammono aldehydes, on carboxazylic and carbazylic acids and on ammono carbonic acids. Examples of such reactions are represented by the equations,<sup>8</sup>



In accordance with equations (1), (2) and (3) an ammono ethyl alcohol is formed by the reduction respectively of an ammono aldehyde-alcohol, of an aquo-ammono acetic acid and of acetic anammonide. Equation (4) represents the reduction of an ammono aldehyde-ether to an ammono alcohol known as ethylaniline, equation (5) the reduction of an ammono benzoic acid to an ammono benzyl alcohol, equation (6) of an ammono carbonic acid to an ammono methyl alcohol.

**Metal Derivatives of the Amines.** The alkali metals dissolve in methylamine to form solutions just as they do in liquid ammonia

<sup>7</sup> Chablay, *Ann. Chim.*, [9] 7, 469 (1914); Lebeau, *Bull. soc. chim.*, 33, 1093 (1905).

<sup>8</sup> Henle, *Ber.*, 35, 3044 (1902).

excepting that they are far less soluble in the former solvent than in the latter. When metallic potassium is heated in contact with the vapor of methylamine<sup>9</sup> or when a liquid methylamine solution of potassium is allowed to stand in the presence of a metallic catalyst (platinum black or a spiral of iron wire) a monopotassium derivative of methylamine is formed.<sup>10</sup> The reaction involved, which is represented by the equation,  $\text{CH}_3\text{NH}_2 + \text{K} = \text{CH}_3\text{NHK} + \text{H}$ , is similar to that which takes place when metallic potassium acts on methyl alcohol.

Alkali metal ammono alcoholates of the formulas,  $\text{C}_2\text{H}_5\text{NHK}$ ,<sup>11</sup>  $\text{CH}_3\text{NHCs}$ ,  $\text{C}_2\text{H}_5\text{NHCs}$  and  $\text{C}_5\text{H}_{11}\text{NHCs}$ <sup>12</sup> have been prepared.

**Ester Formation.** Looking upon methylamine and dimethylamine as ammono methyl alcohols, and upon acetamidine as an ammono acetic acid it follows that as methyl aquoacetate is formed by the action of aquo methyl alcohol on aquo acetic acid so it might be expected that methyl ammonoacetates of the respective formulas,

- (1)  $\text{CH}_3\text{C}(\text{NH})\text{NHCH}_3 \rightleftharpoons \text{CH}_3\text{C}(\text{NH}_2)\text{NCH}_3$ ,
- (2)  $\text{CH}_3\text{C}(\text{NCH}_3)\text{NHCH}_3$ ,
- (3)  $\text{CH}_3\text{C}(\text{NH})\text{N}(\text{CH}_3)_2$ ,
- (4)  $\text{CH}_3\text{C}(\text{NCH}_3)\text{N}(\text{CH}_3)_2$ ,

would be formed by the action of methylamine and of dimethylamine on acetamidine. Carbazylic acid esters of all four types represented by these formulas are known.

A very large variety of esters has been prepared by the action of amines on aquo acids, on acid anhydrides, on acid anammonides and on acid chlorides, a limited number by the action of amines on acid amidines. A few examples of such reactions, in which the amines function in a manner strictly similar to that of the aquo alcohols, are represented by the following equations.

Amines and acids.

- (1)  $\text{CH}_3\text{COOH} + \text{CH}_3\text{NH}_2 = \text{CH}_3\text{CONHCH}_3 + \text{H}_2\text{O}$
- (2)  $\text{CH}_3\text{CONH}_2 + \text{C}_6\text{H}_5\text{NH}_2 = \text{CH}_3\text{CONHC}_6\text{H}_5 + \text{NH}_3$
- (3)  $\text{C}_6\text{H}_5\text{C}(\text{NH})\text{NHC}_6\text{H}_5 + \text{C}_6\text{H}_5\text{NH}_2 = \text{C}_6\text{H}_5\text{C}(\text{NC}_6\text{H}_5)\text{NHC}_6\text{H}_5 + \text{NH}_3$
- (4)  $\text{HONO} + (\text{CH}_3)_2\text{NH} = (\text{CH}_3)_2\text{N} \cdot \text{NO} + \text{H}_2\text{O}$
- (5)  $\text{HO} \cdot \text{Cl} + \text{CH}_3\text{NH}_2 = \text{CH}_3\text{NH} \cdot \text{Cl} + \text{H}_2\text{O}$

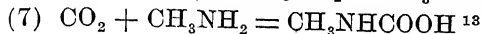
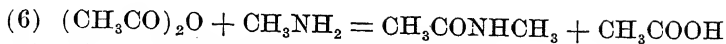
<sup>9</sup> Titherly, *J. Chem. Soc.*, 71, 460 (1897).

<sup>10</sup> Unpublished observations.

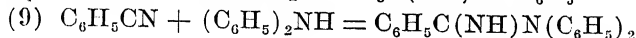
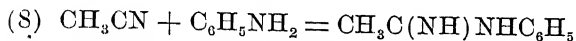
<sup>11</sup> Titherly, *J. Chem. Soc.*, 71, 463 (1897).

<sup>12</sup> Rengade, *Ann. chim. phys.*, [8] 11, 348 (1907).

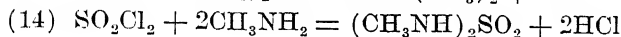
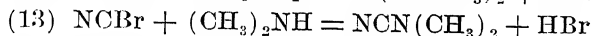
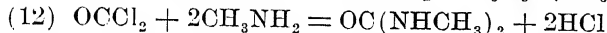
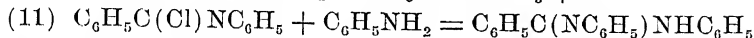
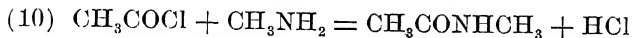
Amines and acid anhydrides.



Amines and acid anammonides.



Amines on acid chlorides.



Equations (1) to (5) inclusive represent the action of amines on the respective acids to form, (1), an N-methyl aquo-ammono-acetate, (2), an N-phenyl aquo-ammono-acetate, (3), an N-N'-diphenyl aquo-ammono-benzoate, (4), an N-N-dimethyl aquo-ammono-nitrite and (5), a methyl ammonohypochlorite. Equations (6) and (7) represent the action of methylamine on acetic anhydride to form an N-methyl aquo-ammono-acetate and on carbonic anhydride to form an N-methyl aquo-ammono-carbonate. Equations (8) and (9) represent the action of ammono phenols on acid anammonides to form carbazylie acid esters. The remaining equations represent the action of amines on acid halides to form, (10), an N-methyl aquo-ammono-acetate, (11), an N-N'-diphenyl ammonobenzoate, (12), an N-N' dimethyl aquo-ammono-carbonate, (13), an N-N-dimethyl ammonocarbonate and (14), an N-N'-dimethyl aquo-ammono-sulfate.

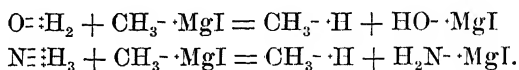
**Acetal Formation.** Just as aldehydes react with the ordinary alcohols to form acetals so also are acetals formed by the interaction of aldehydes with amines. Examples of acetals thus formed will be discussed in the following chapter.

**Grignard Reactions.** The action of alkylmagnesium halides on primary and secondary amines resembles that of the same reagents on aquo alcohols.

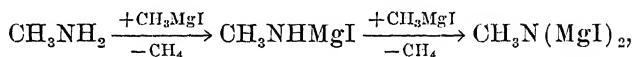
When methylmagnesium iodide is formed by the interaction of metallic magnesium and methyl iodide it is reasonable to assume, in accordance with the equation,  $\text{Mg} + \text{CH}_3\cdot\text{I} = \text{CH}_3\cdot\text{MgI}$ , that

<sup>13</sup> Isolated in the form of its methylammonium salt.

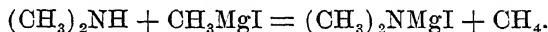
zero valent magnesium is augmented (deelectronized) to an unknown extent and that at the same time the methyl group is reduced to a condition approximately that in which it is present in methane. On such an assumption the action of water and of ammonia on methylmagnesium iodide may be said to involve the solvolysis of a methanobasic magnesium iodide<sup>14</sup> in the one case to an aquobasic salt, in the other to an ammonobasic salt as represented by the equations,



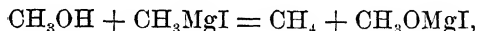
According to Sudborough and Hibbert<sup>15</sup> the action of methylamine on methylmagnesium iodide takes place in two steps,



its action on dimethylamine in accordance with the equation,



Comparing these equations with



which represents the action of methylmagnesium iodide on methyl alcohol the close similarity in the behavior of the alcohols, the primary amines and the secondary amines will be obvious. Trimethylamine being an ether does not react with Grignard reagents.

**Augmentation of the Alkyl Amines.** Since it is in their behavior toward oxidizing agents that the aquo alcohols and ethers exhibit some of their most characteristic properties it is important to show that the amines closely resemble their water analogs in their action toward augmenting agents—that is to say either oxidizing or nitridizing agents—in order to establish them as alcohols and ethers of the nitrogen system.

**Nitridation in Liquid Ammonia Solution.** No systematic investigations have been undertaken with the object in view of determining the extent to which it may be possible to realize experimentally by means of reactions carried out in liquid ammonia solutions, the many nitridizing reactions implied in Table 10 (p. 219). It does happen, however, that the following significant observations have been made.

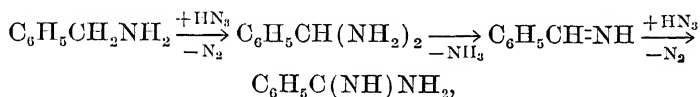
<sup>14</sup> Franklin, *J. Am. Chem. Soc.*, **46**, 2146 (1924).

<sup>15</sup> Sudborough and Hibbert, *J. Chem. Soc.*, **95**, 477 (1909).

In the course of an experimental study of the nitridizing action of hydrazoic acid Chuck<sup>16</sup> found that guanidine is obtained when a liquid ammonia solution containing methylamine and ammonium azide is heated for a time at 100°. An ammono methyl alcohol is thereby nitridized to an ammono carbonic acid,

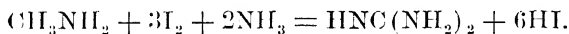


Chuck found furthermore that a fair yield of benzamidine is obtained when a liquid ammonia solution of benzylamine together with an excess of ammonium azide is heated. Although benzylideneimine was not isolated it may be assumed that the reactions involved take place in accordance with the scheme,

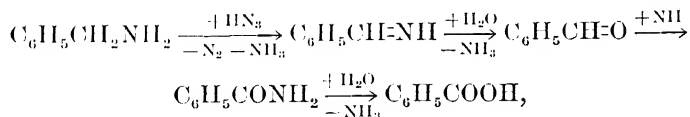


which represents the nitridation of an ammono benzyl alcohol first to an ammono benzaldehyde-alcohol and thence to an ammono benzoic acid, ammono nitric acid functioning as nitridizing agent.

Under the action of iodine in liquid ammonia solution methylamine is converted into guanidine (*cf.* Chapter X) which is to say that an ammono methyl alcohol is augmented to an ammono carbonic acid in accordance with the equation,



**Nitridation in Water Solution.**<sup>17</sup> By boiling a water solution of benzylamine and sodium azide made acid by the addition of sulfuric acid Chuck obtained good yields of aquo benzaldehyde and aquo benzoic acid. The reactions involved may reasonably be represented by the scheme,



in accordance with which it is assumed that benzylamine is nitridized to benzylideneimine which is immediately hydrolyzed to benzaldehyde. This aquo aldehyde is then nitridized to benzamide

<sup>16</sup> Faw Yap Chuck, Thesis, Stanford University, 1925.

<sup>17</sup> Nitridation is used here rather than augmentation or oxidation for the reason that the active agent is ammono nitric acid.

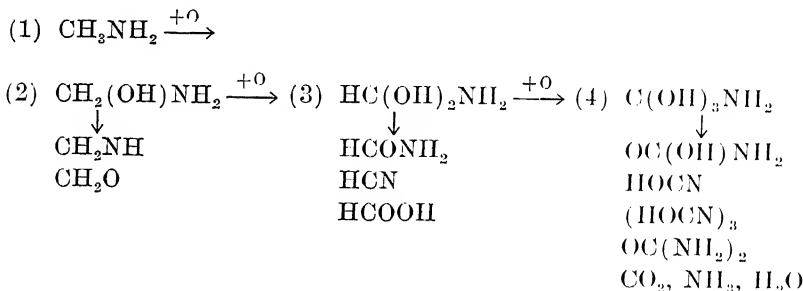


which in hot dilute sulfuric acid solution is hydrolyzed to aquo benzoic acid and ammonia.

**Oxidation of Alkylamines in Water Solution.**<sup>18</sup> Earlier in the chapter it was pointed out that just as methyl alcohol, isopropyl alcohol and tertiary butyl alcohol are respectively a primary, a secondary and a tertiary alcohol so methylamine,  $\text{CH}_3\text{NH}_2$ , and dimethylamine,  $\text{CH}_3\text{NHCH}_3$ , are to be looked upon as primary ammono alcohols, isopropylamine,  $(\text{CH}_3)_2\text{CHNH}_2$ , and diisopropylamine,  $(\text{CH}_3)_2\text{CNHC}(\text{CH}_3)_2$ , as secondary ammono alcohols and tertiary butylamine,  $(\text{CH}_3)_3\text{CNH}_2$ , and ditertiary butylamine,  $(\text{CH}_3)_3\text{CNHC}(\text{CH}_3)_3$ , as tertiary ammono alcohols.<sup>19</sup>

It will be shown in what follows that this classification of the amines into primary, secondary and tertiary ammono alcohols is justified by the known behavior of representatives of each class of compounds toward oxidizing agents in water solution.

**Primary Ammono Alcohols. Methylamine. 1. Oxidation of Carbon.** Assuming the action of oxidizing agents on methylamine to consist in the successive injection of oxygen atoms into positions between the carbon atom and a hydrogen atom in the methyl group as represented by the top horizontal row below it follows that one might expect to find the compounds formulated among the oxidation products of methylamine,



excepting that the compounds represented by the formulas, (2), (3) and (4) are incapable of existence, that methyleneimine would either hydrolyze to aquo formaldehyde and ammonia or undergo deammonation and polymerization to form hexamethylenetetramine

<sup>18</sup> The reactions to be discussed in the remaining portion of this chapter are, with one or two exceptions, brought about by the action of oxidizing agents using the term oxidizing agent in its specific sense as a purveyor of oxygen. In this sense we speak of the oxidation of the amines.

<sup>19</sup> In order to avoid confusion in our discussion of the primary, secondary and tertiary ammono alcohols we shall henceforth simply abandon entirely the use of the terms primary, secondary and tertiary amines when we have occasion to speak of the monoalkyl, dialkyl and trialkyl derivatives of ammonia.

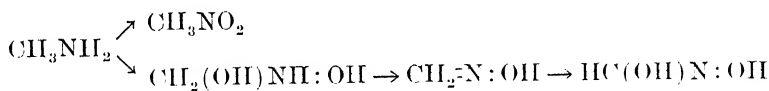
and that only those carbonic acids would appear which are not too readily hydrolyzable.

Of the compounds thus predicted formaldehyde, formic acid, hydrocyanic acid and carbon dioxide and ammonia have been obtained by the action of oxidizing agents on methylamine, cyanuric acid and urea by the oxidation of formamide, cyanic acid and urea by the oxidation of hydrocyanic acid. All these compounds may be regarded as oxidation products of methylamine.

So similarly acetaldehyde, acetonitrile, acetic acid, carbon dioxide and ammonia have been found among the products formed by the action of oxidizing agents on ethylamine. Furthermore acetamide has been obtained by the action of ammonium persulfate on acetaldehyde. The behavior of methylamine and ethylamine toward oxidizing agents closely resembles that of the primary aquo alcohols.

2. *Oxidation of Amine Nitrogen.* Since ammonia is susceptible to oxidation, finally to nitric acid, it may well happen when methylamine is exposed to the action of certain oxidizing agents that the nitrogen atom instead of the carbon atom of the amine will be attacked, or it may even happen that both the carbon and nitrogen will be oxidized either simultaneously or successively.<sup>20</sup>

The observed formation of nitromethane, formaldoxime and formhydroxamic acid by the action of Caro's acid on methylamine and of nitroethane, acetaldoxime and acethydroxamic acid by the oxidizing action of the same reagent on ethylamine is in agreement with these surmises. Representing the formation of nitromethane, formaldoxime and formhydroxamic acid by means of the scheme,



one may say that nitromethane is formed by the oxidation of amine nitrogen to a nitro group, that formaldoxime is formed by way of the unknown compound,  $\text{HO}-\text{CH}_2-\text{NH}:\text{OH}$ , by the simultaneous oxidation of methyl alcohol carbon to formaldehyde carbon and of ammonia nitrogen to hydroxylamine nitrogen, and that formhydroxamic acid is formed from formaldoxime by the oxidation of formaldehyde carbon to formic acid carbon.

Bamberger and Schuetz<sup>21</sup> identified benzaldehyde, benzoic acid, benzonitrile, benzaldoxime, benzhydroxamic acid and phenylnitro-

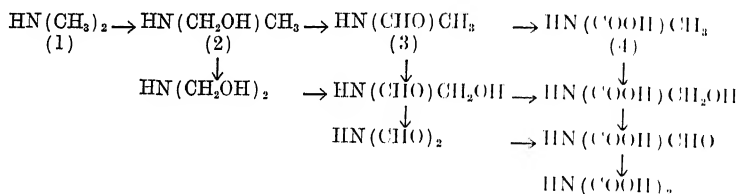
<sup>20</sup> It will be recalled that methyl mercaptan, which is a thio alcohol, behaves toward oxidizing agents in a manner fundamentally different from that of the analogous aquo alcohol in that it is the sulfur instead of the carbon atom which is attacked. Methyl mercaptan is oxidized to methyl sulfonic acid and not to thio formaldehyde.

<sup>21</sup> Bamberger and Schuetz, *Ber.*, **34**, 2262 (1901).

methane among the products formed by the oxidizing action of Caro's acid on benzylamine. Benzamide and phenylnitrolic were also supposed to be present but were not positively identified. In the light of the preceding discussion it will be clear that benzaldehyde, benzoic acid and benzonitrile are products of the augmentation of the alcohol carbon atom contained in benzylamine, that benzaldoxime and benzhydroxamic acid result from the augmentation of both the carbon atom and the nitrogen atom and that in the conversion of benzylamine into phenylnitromethane it is the nitrogen atom only which undergoes augmentation.

**Oxidation of Dimethylamine,  $(\text{CH}_3)_2\text{NH}$ .** Like methylamine this compound is a primary ammonio alcohol. Containing however two methyl alcohol groups, either one or both of which may be augmented to aldehyde, carbylic acid and carbonic acid groups, it may properly be designated as a diprimary ammonio alcohol.

**Oxidation of Carbon.** On the assumption that a properly chosen oxidation agent attacks the carbon atoms only, one may speculate to the effect that some or all of the compounds represented in the following scheme should result from the oxidation of dimethylamine.



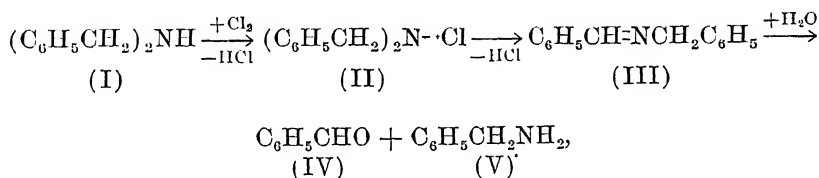
All the compounds thus formulated, leaving aside the question of which are known and which are unknown, would be expected either to break down or undergo hydrolysis in the presence of water, acids or alkalis, as follows: (2) into methylamine and formaldehyde, (3) into methylamine and formic acid, (4) into methylamine and carbon dioxide, (5) into formaldehyde and ammonia, (6) into formaldehyde and formamide or formaldehyde, formic acid and ammonia, (7) into formaldehyde, carbon dioxide and ammonia, (8) into formic acid and ammonia, (9) into formic acid, carbon dioxide and ammonia and (10) into carbon dioxide and ammonia. Other possible decomposition products are here ignored. In view of the above considerations and recalling our discussion of the action of oxidizing agents on mono methylamine it appears that under conditions of effective hydrolytic action the products which one might expect to obtain by the action of oxidizing agents on the two ammonio methyl alcohols in water solution—exclusive of course of the compounds formed by the oxidation of amine nitrogen—are

methylamine, formaldehyde, formamide, aquo formic acid, carbonic anhydride and ammonia.

In harmony with these speculations concerning the action of oxidizing agents on the dialkylamines are the following experimental observations.

1. Dunstan and Goulding<sup>22</sup> obtained formaldehyde and formic acid, together with nitrous acid as products of the action of hydrogen peroxide on dimethylamine.<sup>23</sup>

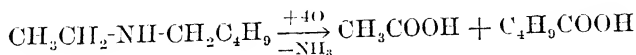
2. Limpricht<sup>24</sup> obtained benzaldehyde and benzylamine by the action of chlorine on dibenzylamine, the reactions involved presumably taking the course,



in accordance with which the dibenzyl ammonohypochlorite (II), formed by the action of chlorine on dibenzylamine (I), by intramolecular augmentation of one of the benzyl alcohol groups to a benzaldehyde group and reduction of hypochlorous acid chlorine to hydrochloric acid chlorine, is converted into the benzaldehyde-ether (III) which undergoing hydrolysis yields benzaldehyde and benzylamine.

3. De Haas<sup>25</sup> found six dialkylamines, including dimethylamine, to give good yields of monoalkylamines when oxidized by means either of potassium permanganate or of potassium ferricyanide. Aquo aldehydes and carboxylic acids were presumably formed at the same time though their presence among the reaction products is not mentioned.

4. It was observed many years ago<sup>26</sup> that chromic acid oxidizes ethylamine quantitatively to acetic acid and valeric acid. Ignoring probable intermediate steps the action of the oxidizing agent may be summarized by means of the scheme,



<sup>22</sup> Dunstan and Goulding, *J. Chem. Soc.*, **75**, 1009 (1890).

<sup>23</sup> It will be recalled that nitrous acid is a product of the action of hydrogen peroxide on ammonia.

<sup>24</sup> Limpricht, *Ann. Chem.*, **144**, 316 (1867).

<sup>25</sup> De Haas, *Rec. trav. chim.*, **14**, 166 (1898).

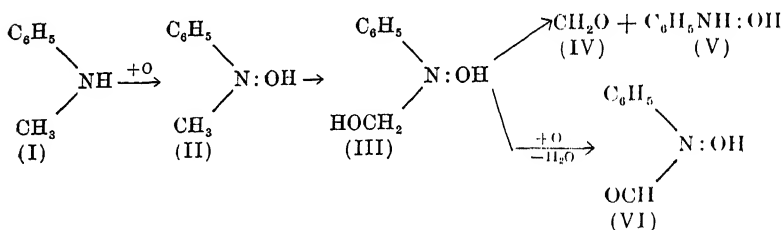
<sup>26</sup> Wanklyn and Chapman, *J. Chem. Soc.*, **4**, 328 (1866); Chapman and Thorp, *ibid.*, **4**, 477 (1866). These observations are not registered in Beilstein, 4th Ed.

which represents the oxidation of the ethyl group of a diprimary ammono alcohol to acetic acid, and of the amyl group to valeric acid.

*Oxidation of Nitrogen.* Among the oxidation products of dimethylamine none beyond a small amount of nitrous acid is known to result from the oxidation of the imide group. However, N-N-diethylhydroxylamine has been obtained by the action of hydrogen peroxide on diethylamine.<sup>27</sup> The reaction, which is represented by the equation,  $(C_2H_5)_2NH + O = (C_2H_5)_2N:OH$ , involves the oxidation of ammonia nitrogen to the state in which it exists in hydroxylamine. In a similar manner dipropylamine has been oxidized to N-N-dipropylhydroxylamine.

*Oxidation of Carbon and Nitrogen.* Phenylhydroxylamine, formylphenylhydroxylamine and formaldehyde have been found among the products of the action of Caro's acid on methylaniline which may be regarded as a mixed primary-tertiary ammono alcohol. Methylaniline is a mixed ammono alcohol ammono phenol.<sup>28</sup>

The reactions involved in the formation of these compounds may be summarized by means of the scheme.



It is assumed that the reactions begin with the oxidation of methylaniline (I) to phenylmethylhydroxylamine (II) after the manner of the oxidation of diethylamine to N-N-diethylhydroxylamine as explained above and that then the methyl carbon of this apparently unknown compound is oxidized to form the formaldehyde phenylhydroxylamine (III) which breaks down to formaldehyde (IV) and phenylhydroxylamine (V). At the same time a portion of this oxime (III) which has been given the name hydroxymethylphenylhydroxylamine, undergoes further oxidation of the aliphatic carbon atom to yield formylphenylhydroxylamine (VI). It is clear that in principle the reactions represented by this scheme consist of the oxidation of an ammono methyl alcohol to formaldehyde, formic

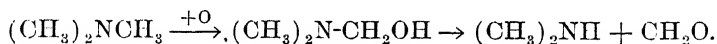
<sup>27</sup> Dunstan and Goulding, *J. Chem. Soc.*, 75, 1009 (1899).

<sup>28</sup> Bamberger and Vuk, *Ber.*, 35, 703 (1902); Bamberger and Tschirner, *Ber.*, 35, 714 (1902); Hübner, *Ber.*, 35, 731 (1902).

acid and hydroxylamine. It is unnecessary to concern ourselves here with six further compounds obtained by Bamberger and Vuk by the action of Caro's acid on methylaniline other than to say that the formation of each may be explained as resulting from the oxidation of methylaniline regarded as a mixed primary-tertiary ammono alcohol.

**Ammono Ethers.** As ethers of the nitrogen system the trialkylamines should behave toward oxidizing agents in a manner resembling more or less closely the familiar action of oxidizing agents on the aquo ethers and on the mono-alkyl and dialkylamines as discussed above. As a matter of fact such is found to be the case.

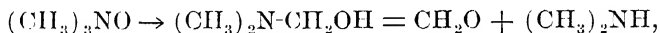
*Trimethylamine.* Dimethylamine, dimethylaminomethanol and formaldehyde have been observed as products of the action of oxidizing agents on trimethylamine.<sup>29</sup>



Dimethylaminoethanol, it may be noted, is an acetal.

The one known oxidation product of trimethylamine containing oxidized nitrogen is trimethylamineoxide,  $(\text{CH}_3)_3\text{NO}$ , which is formed by the action of hydrogen peroxide on trimethylamine.

When heated with aqueous sulfuric acid trimethylamineoxide breaks down to form dimethylamine and formaldehyde, a transformation,



which clearly consists in the intramolecular oxidation of one of the methyl groups to a formaldehyde group and the simultaneous reduction of oxidized nitrogen to ammonia nitrogen.<sup>30</sup>

Diethylamine, acetaldehyde, acetic acid, oxalic acid, carbon dioxide, triethylamineoxide, ammonia and nitric acid have been found among the products of the action of oxidizing agents on triethylamine.<sup>31</sup> All these compounds are readily explained as resulting from the oxidation of the ethyl alcohol groups and the ammonia nitrogen contained in triethylamine.

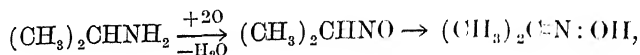
**Secondary Ammono Alcohols,  $\text{R}_2\text{CHNH}_2$ .** Apparently the only known oxidation product of the simplest secondary ammono alcohol is acetoxime which has been obtained by the action of Caro's acid

<sup>29</sup> *Chem. Zentr.*, 1913, II, 1832; 1914, I, 203, 509; Meisenheimer, *Ber.*, 46, 1156 (1913).

<sup>30</sup> Dunstan and Goulding, *J. Chem. Soc.*, 75, 1005 (1899).

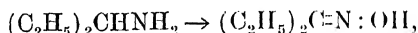
<sup>31</sup> Dunstan and Goulding, *loc. cit.*; Dar Juan, *Am. Chem. J.*, 43, 3 (1910); Meisenheimer, *Ber.*, 46, 1157 (1913).

on isopropylamine.<sup>32</sup> It may be assumed that the reactions involved take place in accordance with the scheme,

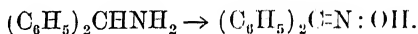


which represents the secondary ammono alcohol as undergoing oxidation to isopropyl nitrosamine, which, undergoing intramolecular oxidation and reduction, rearranges to the dimethylketoxime.

Bamberger and Seligmann observed also that diethylketoneoxime is a product of the oxidation of diethylmethylaniline,

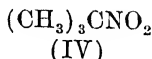
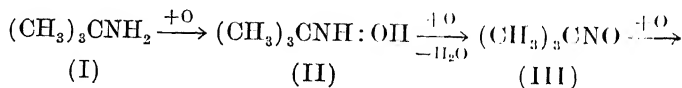


and that benzophenoneoxime is formed in a similar manner by the oxidation of benzhydramine,



Among the products of the action of Caro's acid on phenylmethylethylamine,  $(\text{C}_6\text{H}_5)(\text{CH}_3)\text{CHNH}_2$ , Bamberger and Seligmann identified acetophenoneoxime, acetophenone, phenylethyl nitromethane,  $(\text{C}_6\text{H}_5)(\text{CH}_3)\text{CHNO}_2$ , phenol, acetic acid, formic acid, benzoic acid and carbon dioxide. The appearance of all these compounds may be readily explained as resulting from the oxidation of phenylethylethylamine looked upon as an ammono secondary alcohol.

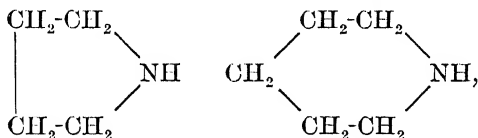
**Tertiary Ammono Alcohols.** Trimethylmethylaniline,  $(\text{CH}_3)_3\text{CNH}_2$ , is a nitrogen analog of tertiarybutyl alcohol, and since both compounds contain the same difficultly oxidizable trimethylmethyl alcohol group one would expect to find the former, in so far as the oxidation of carbon is concerned, offering the same resistance to the action of oxidizing agents as is well known to characterize ordinary tertiarybutyl alcohol. On the other hand there being no apparent reason why the nitrogen of the amine group should resist oxidation one might well expect to find the compounds formulated herewith among the oxidation products of this tertiary ammono alcohol.



<sup>32</sup> Bamberger and Seligmann, *Ber.*, **36**, 701 (1903).

As a matter of fact trimethylmethylhydroxylamine (II), nitroso-trimethylmethane (III) and nitrotrimethylmethane (IV) have been obtained by the oxidizing action of Caro's acid on trimethylmethylamine, as have also the amylhydroxylamine,  $C_2H_5(CH_3)_2CNH:OH$ , the nitrosopentane,  $C_2H_5(CH_3)_2CNO$ , and the nitropentane,  $C_2H_5(CH_3)_2CNO_2$ , by the action of Caro's acid on dimethylethylmethylamine.<sup>33</sup> It is interesting to recall in this connection that aniline, which may be regarded as a tertiary ammono alcohol, has been oxidized successively to phenylhydroxylamine, nitrosobenzene and nitrobenzene.

**Cyclic Ammono Alcohols.** Pyrrolidine and hexahydropyridine,



and other heterocyclic nitrogen compounds show the properties of ammono alcohols.

<sup>33</sup> Bamberger and Seligmann, *Ber.*, 36, 685 (1903).



## CHAPTER XXVI.

### ALDEHYDE-ALCOHOLS, ALDEHYDE-ETHERS, ALDEHYDE-ACETALS AND ALDEHYDE-ESTERS.

The formulas, (1)  $\text{RCH}(\text{OH})_2$ , (2)  $\text{RCH}=\text{O}$ , (3)  $\text{RCH}(\text{OH})\text{OR}'$ , (4)  $\text{RCH}(\text{OH})\text{O}-\text{OCR}'$ , (5)  $\text{RCH}(\text{OR}')_2$ , (6)  $\text{RCH}(\text{O}-\text{OCR}')_2$ , represent (1) aldehyde hydrates, (2) aldehydes, and (3), (4), (5) and (6) acetals respectively.<sup>1</sup>

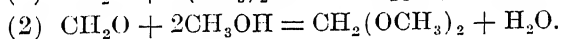
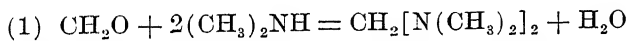
Looking upon these compounds as derivatives of water and speculating upon the existence of analogous compounds belonging to the nitrogen system we find that the trivalency of nitrogen makes possible the preparation of compounds represented by the following formulas, (1)  $\text{RCH}(\text{NH}_2)_2$ , (2)  $\text{RCH}(\text{NH}_2)\text{NHR}'$ , (3)  $\text{RCH}(\text{NHR}')_2$ , (4)  $\text{RCH}(\text{NH}_2)\text{NR}'_2$ , (5)  $\text{RCH}(\text{NHR}')\text{NR}'_2$ , (6)  $\text{RCH}(\text{NR}'_2)_2$ , (7)  $\text{RCH}=\text{NH}$ , (8)  $\text{RCH}=\text{NR}'$  and (9)  $\text{RCH}(\text{N}-\text{CHR}')_2$ , in which R represents a hydrogen atom, an alkyl or an aryl group and R' either a hydrocarbon radical or an ammonio acid residue.

The first formula represents nitrogen analogs of the aldehyde hydrates. Formulas (2) to (6) inclusive represent compounds which are the nitrogen analogs of the acetals. They may be called ammonio acetals. Compounds represented by formula (7) are ammonio aldehydes and, since the nitrogen atom is associated with an atom of hydrogen, at the same time either an ammonio alcohol or an ammonio acid. It is probably best to regard the alkylideneimines, of which ethylideneimine,  $\text{CH}_3\text{CH}=\text{NH}$ , is an example, as ammonio aldehyde-alcohols. Formula (8) represents compounds which by virtue of the double linkage between the alkylidene group and the nitrogen atom, are aldehydes. When the ammonio alcohol hydrogen in formula (7) is replaced by an alkyl or aryl group an ammonio aldehyde-ether results, when replaced by an acid amidine residue an aldehyde-ester is formed. An example of the former is ethylidene-ethylimine,  $\text{CH}_3\text{CH}=\text{NC}_2\text{H}_5$ , of the latter benzylidenebenzamidine,  $\text{C}_6\text{H}_5\text{CH}=\text{NC}(\text{NH})\text{C}_6\text{H}_5$ . Compounds represented by formula (9), among which for example is the well-known hydrobenzamide,  $(\text{C}_6\text{H}_5\text{CH})_3\text{N}_2$ , are aldehydes in so far as the carbon to nitrogen double bond is concerned while at the same time they are acetals in the sense that they are derivatives of alkylidenediamines even though the groups taking the place of the amine hydrogen atoms

<sup>1</sup> It will be noted that the term acetal is here broadened to include the acid derivatives of the aldehydes.

are aldehyde groups and not alkyl, aryl or acid groups as is the case with the more familiar acetals. Somewhat arbitrarily perhaps we shall speak of the Schiff bases (8) as ammono aldehyde-ethers and of the compounds represented by formula (9) as ammono dialdehyde-acetals. Having gone thus far in expanding our nomenclature it becomes reasonable to apply the term acetalization to the dimerization of the unknown methylene nitride  $(\text{CH}_2)_3\text{N}_2$  to hexamethylenetetramine and the trimerization of acetaldehyde to paraldehyde and to speak of these polymerization products as cyclic acetals.

**Methylenediamine**,  $\text{CH}_2(\text{NH}_2)_2$ , **Methyleneimine**,  $\text{CH}_2=\text{NH}$ , and **Methylene Nitride**,  $(\text{CH}_2)_3\text{N}_2$ . The latter two unknown compounds come as near being the nitrogen analogs of aquo formaldehyde as the trivalency of nitrogen permits. Methylenediamine, which is the nitrogen analog of methylene glycol, is known in water solution,<sup>2</sup> and in the form of its nitrate, hydrochloride and sulfate.<sup>3</sup> Like methylene glycol, it forms a large number of alkyl, aryl, and acyl derivatives which are to be looked upon as acetals. For example, tetramethylmethylenediamine,  $(\text{CH}_3)_2\text{N}-\text{CH}_2-\text{N}(\text{CH}_3)_2$ , is an ammono acetal which is formed by the action of dimethylamine on formaldehyde just as methylal is formed by the action of aquo methyl alcohol on formaldehyde. The parallel reactions are represented by the equations,



This ammono acetal is hydrolyzed by the action of dilute hydrochloric acid to formaldehyde and dimethylamine just as methylal under similar treatment yields formaldehyde and methyl alcohol as represented by the above equation read from right to left.

Acyl derivatives of methylenediamine have also been prepared, such, for example, as diacetyldiaminomethane,  $\text{CH}_2(\text{NHOCCH}_3)_2$ . This compound is a methylene aquo-ammono-acetate. Neither of the methylene ammonoacetates represented by the formulas,  $\text{CH}_2[\text{NH}(\text{NH})\text{CCH}_3]_2$  and  $\text{CH}_2=\text{N}(\text{NH})\text{CCH}_3$ , has been prepared. A benzylidene ammonobenzoate,  $\text{C}_6\text{H}_5\text{CH}=\text{N}(\text{NH})\text{CC}_6\text{H}_5$ , is known.

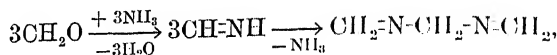
Many alkyl, aryl and acyl derivatives,  $\text{CH}_2=\text{NR}$  and  $\text{CH}_2=\text{NAc}$ , of methyleneimine are known some of which will be discussed later. Methylene nitride is known in its dimeric form as hexamethylenetetramine.

**Hexamethylenetetramine**,  $(\text{CH}_2)_6\text{N}_4$ . The formation of this important compound by the action of ammonia on formaldehyde is readily explained on the assumption that the aquo aldehyde is am-

<sup>2</sup> Einhorn and Mauermayer, *Ann. Chem.*, **343**, 306 (1905).

<sup>3</sup> Knudsen, *Ber.*, **47**, 2698 (1914).

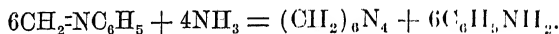
monolyzed by the action of ammonia to methylene nitride, say in accordance with the equation,



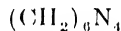
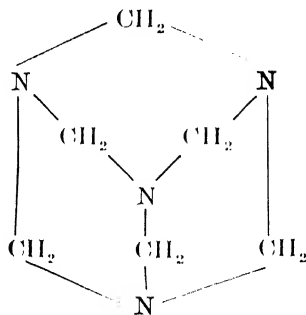
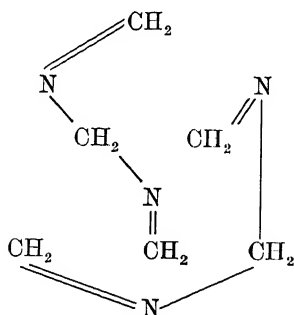
and that the dialdehyde-acetal thus formed immediately dimerizes to hexamethylenetetramine.

Hexamethylenetetramine has also been prepared by the action of ammonia on trioxymethylene, by the action of alcoholic ammonia on methylene chloride at 125° and by warming a liquid ammonia solution of methylene chloride.<sup>5</sup>

Strain has shown furthermore that formaldehydeaniline is ammonolyzed by the action of liquid ammonia to hexamethylenetetramine and aniline as represented by the equation,



The conversion of aquo formaldehyde into trioxymethylene and of methylene nitride into hexamethylenetetramine involve closely similar reactions which in principle are processes of acetalization. In the one case three molecules of methylene oxide unite to form a hexacyclic molecule of two dimensions, so to say, while in the other two molecules of methylene nitride interact to form a three dimensional molecule made up of four hexagonal rings each containing three nitrogen atoms and three methylene groups in alternate positions and with each nitrogen atom held in common by three hexagons and each methylene group by two hexagons. On a plane the dimerization of methylene nitride to hexamethylenetetramine may be represented by the scheme,<sup>6</sup>



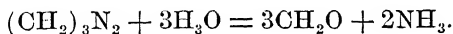
<sup>5</sup> Strain, Thesis, Stanford University (1927).

<sup>6</sup> The close analogy between the two reactions becomes particularly clear when the dimerization of methylene nitride is followed by means of a three dimensional model.

This formula for hexamethylenetetramine was proposed and supported by convincing arguments by Duden and Scharff.<sup>7</sup>

In further support of this formula it is important to note that the three-dimensional symmetry of the hexamethylenetetramine molecule represented by the above formula expresses itself in the crystal form and in the Roentgen ray spectrographs as has been shown by Dickinson and Raymond.<sup>8</sup>

Hexamethylenetetramine itself is of course not an aldehyde any more than is trioxymethylene. Rather it is an exceptionably stable acetal-like compound which develops aldehydic properties only when acted upon by reagents which bring about its depolymerization. Thus the action of aqueous hydrochloric acid in converting hexamethylenetetramine into ordinary formaldehyde may be explained as consisting in the depolymerization of hexamethylenetetramine to methylene nitride,  $(\text{CH}_2)_6\text{N}_4 \rightarrow 2\text{CH}_2=\text{N}-\text{CH}_2-\text{N}=\text{CH}_2$ , followed by the hydrolysis of this dialdehyde-acetal to aquo formaldehyde and ammonia in accordance with the equation,



While Duden and Scharff's formula seems to be fairly well established it must be said that it does not readily lend itself to satisfactory explanations of some of the many reactions into which hexamethylenetetramine has been observed to enter.

**Ethylideneimine,  $\text{CH}_3\text{CH}=\text{NH}$ .** *Formation.* When aldehyde ammonia is allowed to stand in vacuum over concentrated sulfuric acid it loses water and yields trimolecular ethylideneimine which may be looked upon as paraldehyde in which the three oxygen atoms are replaced by imide groups.<sup>9</sup>

In this laboratory trimolecular ethylideneimine has been obtained beautifully crystallized by dehydrating aldehyde ammonia in solution in liquid ammonia by means of calcium amide, decanting the solution from the insoluble mixture of calcium amide and calcium hydroxide and evaporating to crystallization.<sup>10</sup>

By heating the vapor of trimolecular ethylideneimine to temperatures around  $260^\circ$  and condensing at  $-35^\circ$ , Strain was able to obtain the monomolecular modification as a mobile liquid which after a time at laboratory temperature reverts to the trimolecular form.

It is interesting to note that as acetaldehyde in water solution is converted into so-called aldehyde resin by the action of potassium hydroxide so, as observed by Strain, potassium amide when added

<sup>7</sup> Duden and Scharff, *Ann. Chem.*, **288**, 218 (1895).

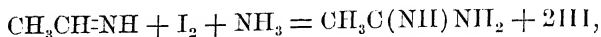
<sup>8</sup> Dickinson and Raymond, *J. Am. Chem. Soc.*, **45**, 22 (1923).

<sup>9</sup> Delépine, *Ann. Chim.*, [7] **16**, 103 (1899).

<sup>10</sup> Strain, *J. Am. Chem. Soc.*, **54**, 1225 (1932).

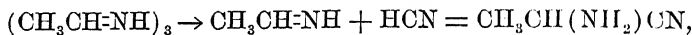
to a liquid ammonia solution of ethylideneimine brings about the formation of dark-colored condensation products.

*Augmentation.* Strain found that trimolecular ethylideneimine is converted into acetamidine by the action of iodine in liquid ammonia solution. The reaction involved, which may be represented by the equation,



clearly consists in the nitridation of an ammono acetaldehyde alcohol to an ammono acetic acid. Whether depolymerization precedes nitridation as has been assumed in writing the above equation or whether trimolecular ethylideneimine is nitridized to an unknown and presumably unstable trimer of acetamidine, one cannot say.

*Action of Hydrocyanic Acid.* When trimolecular ethylideneimine suspended in absolute alcohol, is treated with hydrocyanic acid  $\alpha$ -aminopropionitrile is formed<sup>11</sup> in accordance with the equation



which represents a reaction analogous to that which takes place when hydrocyanic acid acts on acetaldehyde.

Delépine found that two further products of the respective formulas,  $[\text{CH}_3\text{CH}(\text{CN})]_2\text{NH}$  and  $[\text{CH}_3\text{CH}(\text{CN})]_3\text{N}_2$ , are formed at the same time. It may be that the latter two compounds result from the deammonation of  $\alpha$ -aminopropionitrile.

*Hydracetamide, Ethylidene Nitride,  $(\text{CH}_3\text{CH})_3\text{N}_2$ ,* which may be regarded as a homolog of an hypothetical methylene nitride have not been prepared though little is known concerning its properties.

*Hexaethylidenetetramine,  $(\text{CH}_3\text{CH})_6\text{N}_4$ .* According to Delépine<sup>12</sup> the compound, prepared by Kudernatsch<sup>13</sup> by heating acetaldehyde in aqua ammonia solution, and reported as hexaethylidenetetramine, is identical with tricrotylidenetetramine formed by the interaction of crotonaldehyde and ammonia.

#### BENZYLIDENEIMINE AND HYDROBENZAMIDE

Just as it frequently happens that aromatic compounds lend themselves much more successfully to experimental investigation than do their aliphatic analogs, so, in striking contrast with our comparatively meager knowledge of the action of ammonia on the

<sup>11</sup> Delépine, *Bull. soc. chim.*, [3] 29, 1182 (1903).

<sup>12</sup> Delépine, *Bull. soc. chim.*, [4] 1, 594 (1907).

<sup>13</sup> Kudernatsch, *Monatsh.*, 21, 137 (1900).

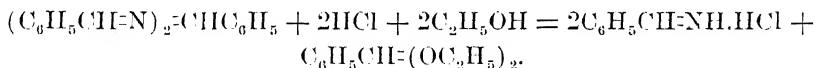
aliphatic aldehydes, very many observations are on record which support the view that the compounds represented by the formulas,  $C_6H_5CH=NH$ ,  $C_6H_5CH=NR$  and  $(C_6H_5CH=N)_2CHC_6H_5$ , are respectively an aldehyde-alcohol, an aldehyde-ether and a dialdehyde-acetal.

**Benzylideneimine**,  $C_6H_5CH=NH$ . Following is an account of observations made, for the most part by Strain,<sup>14</sup> on the preparation and properties of this compound.

*Formation.* Benzylideneimine is formed by allowing hydrobenzamide to stand in contact with liquid ammonia at laboratory temperature. The slightly soluble hydrobenzamide gradually undergoes ammonation to form the very soluble benzylideneimine which may be obtained in the form of beautiful crystals by slow evaporation of the solvent. On exposure to the atmosphere or on standing in vacuum in the presence of an ammonia absorbent, benzylideneimine loses ammonia and passes back into hydrobenzamide. The reactions are represented by the reversible equation,



Busch<sup>15</sup> prepared benzylideneimine in the form of its hydrochloride by treating hydrobenzamide, in solution in a mixture of benzene and ethyl alcohol, with hydrochloric acid gas. The reactions take place in accordance with the equation,



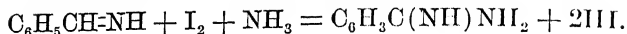
Aquo ethyl alcohol, in the presence of hydrochloric acid, acts on the ammono dialdehyde-acetal to form an ammono aldehyde-alcohol and an aquo acetal.

*Action of Reducing Agents.* In the presence of metallic sodium in liquid ammonia solution benzylideneimine is reduced to benzylamine. At the same time a small amount of toluene is formed. The conversion of benzylideneimine into benzylamine in accordance with the equation,  $C_6H_5CH=NH + 2H = C_6H_5CH_2NH_2$ , is analogous to the reduction of benzaldehyde to benzyl alcohol.

*Action of Augmenting Agents.* Strain obtained benzamidine and cyaphenine by the action of iodine on benzylideneimine in liquid ammonia solution. The formation of benzamidine may be explained as consisting in the conversion of the aldehyde-alcohol into an ammono benzoic acid by the nitridizing action of iodine,

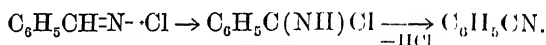
<sup>14</sup> Strain, *J. Am. Chem. Soc.*, **49**, 1558 (1927).

<sup>15</sup> Busch, *Ber.*, **29**, 2144 (1896).



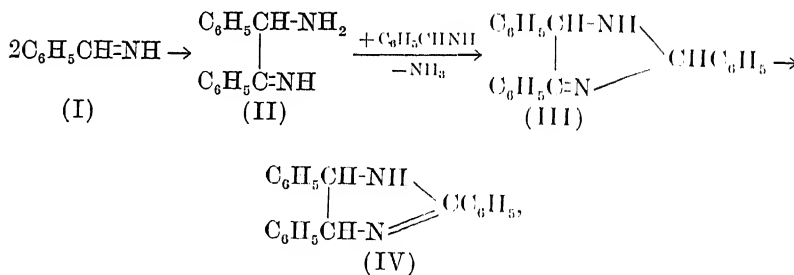
On the assumption that benzylideneimine exists in liquid ammonia solution partly in the trimeric form then the formation of cyanophenine can be explained as taking place in accordance with the equation,  $(\text{C}_6\text{H}_5\text{CH}=\text{NH})_3 + 3\text{NH}_3 = (\text{C}_6\text{H}_5\text{CN})_3 + 3\text{NH}_3$ . Whether however polymerization takes place before or after nitridation is an open question.

When benzylidenechlorimine, which is to be regarded as an ammono benzaldehyde and at the same time an ammono hypochlorous acid ester, is warmed with sodium hydroxide solution, or even with water, benzonitrile and hydrochloric acid are formed as the result of a Beckmann-like rearrangement,



Clearly by the augmenting action of hypochlorous acid chlorine a benzaldehyde derivative is converted into benzoic anammonide.<sup>16</sup>

*Benzoïn Condensation.* Strain found that benzylideneimine slowly goes over into amarine when allowed to stand at laboratory temperature in solution in liquid ammonia. The reactions involved probably take the course (cf. p. 251),

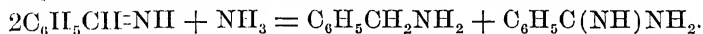
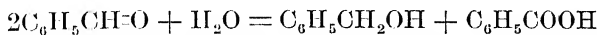


in accordance with which benzylideneimine undergoes the benzoïn condensation to form what may be called an ammono benzoïn (II). This unknown compound reacts with a third molecule of benzylideneimine to form (III) which, undergoing intramolecular augmentation of the benzaldehyde group to a benzoic acid group and reduction of the ketone group to a secondary alcohol group, passes over into amarine (IV).

*Cannizzaro Reactions.* According to Strain, benzylamine, benzamidine and lophine (2-4-5-triphenylimidazole) are formed when

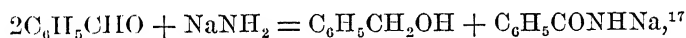
<sup>16</sup> Raschig, "Schwefel- und Stickstoffstudien," Verlag Chem., Leipzig-Berlin, 1924.

benzylideneimine is heated with potassium amide in liquid ammonia solution. The reactions involved in the formation of benzylamine and benzamidine resemble the familiar conversion of aquo benzaldehyde into benzyl alcohol and benzoic acid under the action of aqueous potassium hydroxide. The parallel Cannizzaro reactions are represented by the equations,



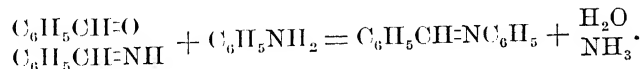
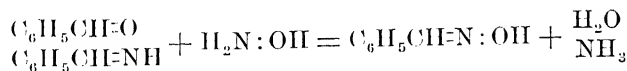
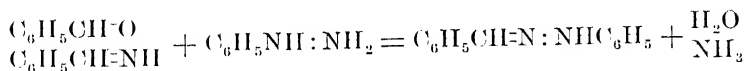
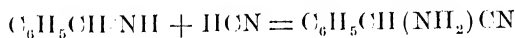
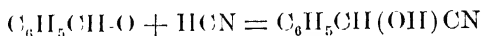
A portion of the benzylideneimine undergoes the benzoin condensation to form amarine which Strain found to yield lophine when heated in liquid ammonia solution with potassium amide.

It is interesting to observe in this connection that aquo benzaldehyde, in benzene solution, under the action of sodium amide, undergoes a Cannizzaro reaction,



to form aquo benzyl alcohol and an aquo-ammono benzoic acid.

*Action of Hydrocyanic Acid, Phenylhydrazine, Hydroxylamine and Aniline.* Strain has furthermore shown that hydrocyanic acid, phenylhydrazine, hydroxylamine and aniline act on benzylideneimine, in liquid ammonia solution, in a manner closely resembling the action of the respective reagents on aquo benzaldehyde in aqueous or alcoholic solution. The analogous reactions take place in accordance with the following equations,



The significance of the reactions thus represented is so obvious as to render comment unnecessary.

*Metallic Salts.* Looking upon benzylideneimine either as an aldehyde-alcohol or as an aldehyde-acid one might expect that in

<sup>17</sup> Haller and Bauer, *Ann. Chim.*, [8] **16**, 150 (1909).



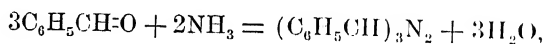
liquid ammonia solution it would react with alkali metal amides to form salts, for example the sodium salt in accordance with the equation,  $C_6H_5CH-NH + NaNH_2 = C_6H_5CH-NNa + NH_3$ . As a matter of fact Strain so prepared sodium benzyldeneimine and potassium benzyldeneimine,  $C_6H_5CH-NK$ . Calcium amide does not dissolve in a liquid ammonia solution of benzyldeneimine which probably means that the acid properties of this compound are too weak to permit the existence of a salt of calcium in the presence of ammonia. Such a salt in solution in liquid ammonia would undoubtedly undergo ammonolytic decomposition with the precipitation of insoluble calcium amide.

Although no definite line can be drawn between alcohols and acids in respect to their ability to form metallic derivatives it seems fair to say that the above considerations tend to support the view already expressed that compounds represented by the formula,  $RCH-NH$ , are aldehyde-alcohols rather than aldehyde-acids.

A discussion of the aldehyde-ethers represented by the formula,  $RCH-NR'$ , known as Schiff bases, is taken up later.

**Hydrobenzamide**,  $(C_6H_5CH-N)_2CHC_6H_5$ . In the following pages a fairly complete case is made in support of the view that hydrobenzamide is an ammono benzaldehyde in so far as doubly bonded carbon to nitrogen is concerned and that in respect to the third benzaldehyde group attached by way of the two nitrogen atoms to the rest of the molecule it is an acetal. We venture to call hydrobenzamide a dibenzaldehydebenzyldene-acetal.

*Formation and Hydrolysis.* The formation of hydrobenzamide by the action of ammonia on aquo benzaldehyde in accordance with the equation,



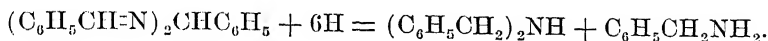
is to be looked upon as involving the ammonolysis of aquo benzaldehyde to an ammono benzaldehyde-acetal, while the reciprocal conversion of hydrobenzamide into benzaldehyde, as represented by the same equation read from right to left, consists in the hydrolysis of the ammono aldehyde-acetal to aquo benzaldehyde. A benzaldehyde ammonia of the formula,  $(C_6H_5CH)_2(OH)(NH)NH_2$ , is also known.

*Action of Augmenting Agents.* By heating hydrobenzamide in liquid ammonia solution with ammonium azide fair yields of lophine and phenyl cyanide are obtained.<sup>18</sup> Phenyl cyanide which is the anammonide of benzoic acid is formed by the nitridizing action of ammono nitric acid on the benzaldehyde-acetal. Lophine has long been known as a product of the oxidation of hydrobenzamide.

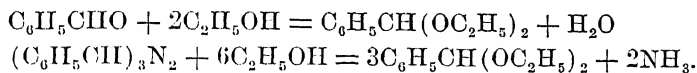
<sup>18</sup> Chuck, Thesis, Stanford University, 1925.

By the action of iodine and sodium carbonate on hydrobenzamide in benzene solution phenyl cyanide is obtained in its trimolecular form.<sup>19</sup>

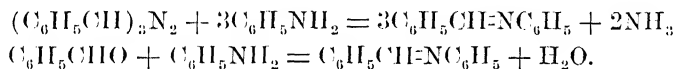
*Action of Reducing Agents.* Hydrobenzamide is easily reduced,<sup>20</sup> not to a single primary alcohol, however, as is the case with aquo benzaldehyde and with benzylideneimine, but to a mixture of two primary ammono alcohols, namely benzylamine and dibenzylamine, in a manner represented by the equation,



*Action of Alcohol.* Just as aquo benzaldehyde is acted upon by ethyl alcohol in the presence of hydrochloric acid to form benzylidenediethylacetal and water, so hydrobenzamide on similar treatment is converted into the same acetal and ammonia.<sup>21</sup> The close parallelism between the respective reactions is shown by the equations,

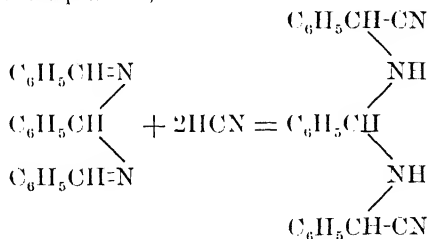


*Action of Aniline.* Many amines act on hydrobenzamide to yield products identical with those formed by the action of the same amines on aquo benzaldehyde. Aniline, for example, reacts with hydrobenzamide and with aquo benzaldehyde as represented by the parallel equations,<sup>22</sup>



Benzylideneaniline, which is formed, is an ammono aldehyde-ether.

*Action of Hydrocyanic Acid.* Hydrobenzamide forms an addition product with two molecules of hydrocyanic acid<sup>23</sup> in the manner represented by the equation,



<sup>19</sup> Robin, *Ann. Chim.*, [9] **16**, 113 (1921); Busch, *Ber.*, **29**, 2144 (1896).

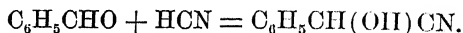
<sup>20</sup> Fischer, *Ann. Chem.*, **241**, 328 (1887).

<sup>21</sup> Lieke, *Ann. Chem.*, **112**, 303 (1859).

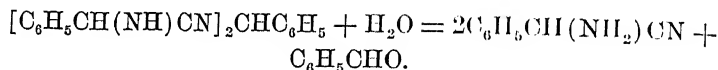
<sup>22</sup> Lachowicz, *Monatsh.*, **9**, 695 (1888).

<sup>23</sup> Plöchl, *Ber.*, **13**, 2118 (1880).

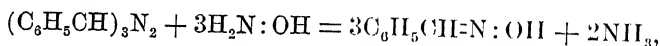
It is clear that the reaction thus represented is closely similar to that which takes place when hydrocyanic acid acts on ordinary benzaldehyde to form mandelic acid nitrile,



The latter compound is a simple cyanhydrine. The former, in so far as the two  $\text{C}_6\text{H}_5\text{CH}(\text{NH})\text{CN}$  groups are concerned, is a cyanamine. The hydrobenzamide hydrocyanic acid addition product is at the same time an ammono acetal and is accordingly easily hydrolyzed by the action of dilute hydrochloric acid to aquo benzaldehyde and benzyldienecyanamine,

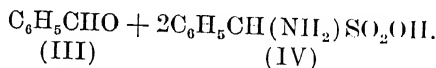
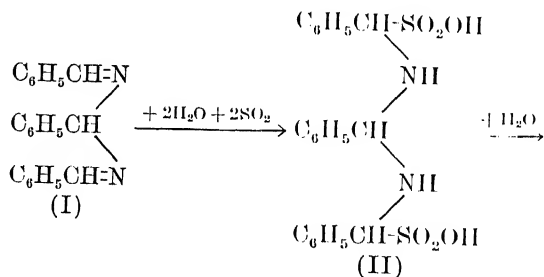


*Action of Hydroxylamine.* The action of hydroxylamine on hydrobenzamide, which may be represented by the equation,



is closely similar to its action on aquo benzaldehyde. Benzaldoxime is formed in each case; in the first with the elimination of ammonia, in the latter of water.<sup>24</sup>

*Action of Sulfurous Acid.* By dissolving hydrobenzamide in benzene, adding two molecules of water per molecule of the dialdehyde-acetal and then shaking the mixture while passing a current of sulfur dioxide a sulfurous acid addition product is formed as represented by the first step in the following scheme,<sup>25</sup>

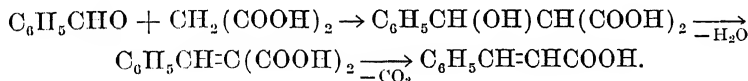


<sup>24</sup> Lachowicz, *Ber.*, 22, 2888 (1889).

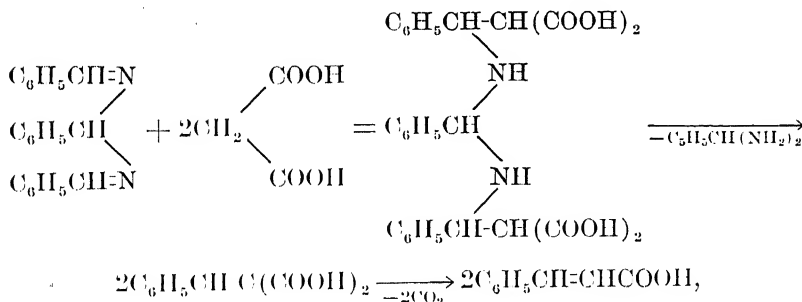
<sup>25</sup> H. van de Griendt, Thesis, Stanford University (1926). Cf. Strain, *J. Am. Chem. Soc.*, 49, 157 (1927); Otto, *Ann. Chem.*, 112, 305 (1859).

This addition product (II) is hydrolyzed by the action of water to aquo benzaldehyde and a compound (IV) which is obviously the ammonia analog of the benzaldehyde aquo sulfurous acid addition product,  $C_6H_5CH(OH)SO_2OH$ . This latter compound is known only in the form of its alkali metal salts. The former is stable for the reason, presumably, that it is capable of forming a so-called inner salt.

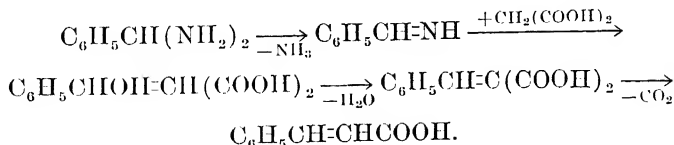
*Action of Malonic Acid.* As cinnamic acid is formed by the action of malonic acid on benzaldehyde so also is it formed by the action of malonic acid on hydrobenzamide.<sup>26</sup> The action of malonic acid on benzaldehyde is usually explained as consisting in an aldol-like condensation followed by loss of water and carbon dioxide to form cinnamic acid as represented by the scheme,



The formation of cinnamic acid by the action of malonic acid on hydrobenzamide takes place in a similar manner. The scheme,

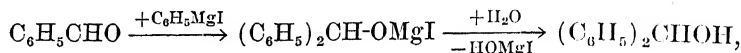


represents, first, an aldol-like condensation taking place between the two ammono aldehyde groups in hydrobenzamide on the one hand and two molecules of malonic acid on the other; second, the decomposition of this hypothetical compound into benzylidenediamine, carbon dioxide and cinnamic acid. By loss of ammonia benzylidenediamine passes over into benzylideneimine which, reacting with malonic acid, gives a third molecule of cinnamic acid,

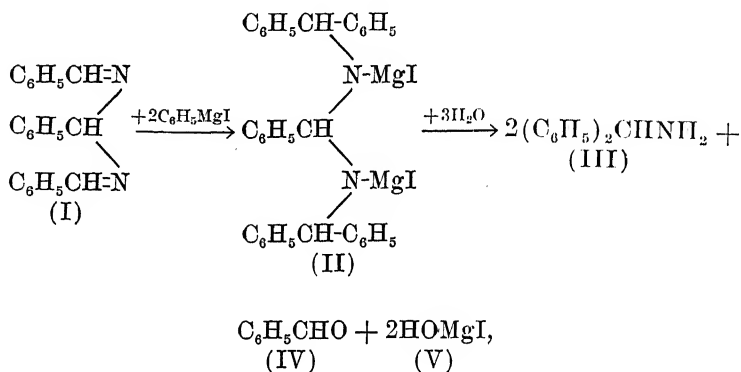


<sup>26</sup> Knoevenagel, *Ber.*, 31, 2596 (1898).

*Action of Phenylmagnesium Iodide.* Just as aquo benzaldehyde is converted into diphenylcarbinol in accordance with the familiar scheme,



so as represented by the analogous scheme,



hydrobenzamide (I) forms with phenylmagnesium iodide an addition product (II) which on treatment with water is hydrolyzed to benzhydrylamine (III), aquo benzaldehyde (IV) and basic magnesium iodide (V).<sup>27</sup>

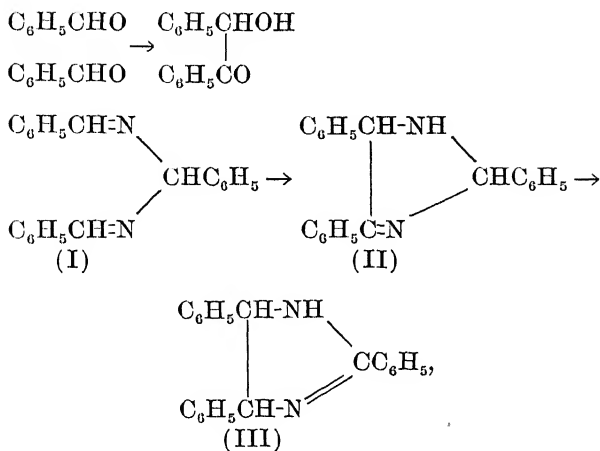
In the one case an aldehyde group is reduced to an alcohol group while at the same time the phenyl group is augmented from the state in which it exists in phenylmagnesium iodide to that in which it is present in the secondary alcohol; in the other two aldehyde groups are reduced simultaneously with the augmentation of two phenyl groups.

*Benzoin Condensation.* It has long been known that hydrobenzamide, when heated, is converted into an isomer known as amarine. More recently it has been shown that the same condensation takes place when hydrobenzamide is treated with a liquid ammonia solution of potassium amide.<sup>28</sup>

Assuming for the moment that amarine has the constitution represented by the formula (II) below it will be clear from an inspection of the equations,

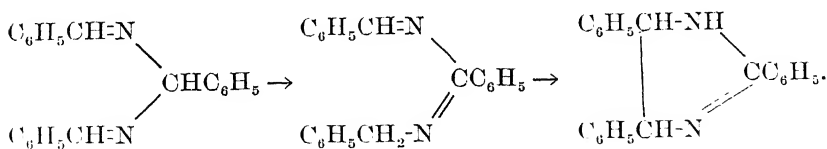
<sup>27</sup> Busch and Leeftelm, *J. prakt. Chem.*, [2] 77, 1 (1908).

<sup>28</sup> Strain, *J. Am. Chem. Soc.*, 49, 1565 (1927).

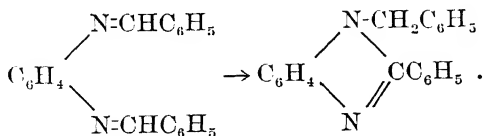


that the formation of benzoin from benzaldehyde and of compound (II) from hydrobenzamide involve closely analogous condensation reactions. In the first case, with the establishment of a carbon to carbon union, two molecules of benzaldehyde are converted into a mixed ketone secondary alcohol. In the second the same carbon to carbon union is established and at the same time a hydrogen atom from one of the aldehyde groups wanders to the nitrogen atom of the other thereby converting the one aldehyde group into a secondary alcohol group and the other into a ketone group.

Since Japp and Moir<sup>29</sup> have shown that amarine has the constitution represented by formula (III) it follows that the transformation of the assumed primary condensation product (II) into amarine involves an intramolecular Cannizzaro reaction. It is possible in the conversion of hydrobenzamide into amarine that a Cannizzaro reaction precedes a benzoin-like condensation,



An interesting example of an intramolecular Cannizzaro reaction is represented by the equation,



<sup>29</sup> Japp and Moir, *J. Chem. Soc.*, 77, 639 (1900).

When dibenzylidene-ortho-phenylenediamine, which is an ammono benzaldehyde-ether closely related to benzylidenephénylimine, is heated above its melting point it undergoes an intramolecular rearrangement which consists in the reduction of one of the benzaldehyde groups to an alcohol group and the simultaneous augmentation of the other to a benzoic acid group. The resulting compound, 2-phenyl-1-benzylbenzimidazole, is a cyclic benzyl-o-phenylene ester of an ammono benzoic acid. It is a benzyl phenylene derivative of benzamidine.<sup>30</sup>

#### SCHIFF'S BASES

Aldehyde-ethers and ketone-ethers of the general formulas,  $\text{CH}_2=\text{NR}$ ,  $\text{RCH}=\text{NR}$ , and  $\text{R}_2\text{C}=\text{NR}$ , in which R represents either alkyl or aryl radicals,<sup>31</sup> constitute a large group of important compounds long recognized as possessing many properties in common with the aldehydes and ketones. The simpler members of the group are prone to polymerization. Methylenemethylimine,  $\text{CH}_2=\text{NCH}_3$ , for example, is known only in its trimeric form, methylenephénylimine,  $\text{CH}_2=\text{NC}_6\text{H}_5$ , polymerizes with the greatest ease, while others, such as benzylidenephénylimine,  $\text{C}_6\text{H}_5\text{CH}=\text{NC}_6\text{H}_5$ , show no such tendency. In general the Schiff bases may be reduced to ammono alcohols,  $\text{RCH}=\text{NR} + 2\text{H} = \text{RCH}_2\text{NHR}$ , and oxidized—excepting those of the formula,  $\text{R}_2\text{C}=\text{NR}$ , which of course are ketones and not aldehydes—to carboxylic acid esters,  $\text{RCH}=\text{NR} + \text{O} = \text{RC}(\text{OH})\text{NR}$ . Many of them have been observed to unite with hydrocyanic acid,  $\text{RCH}=\text{NR} + \text{HCN} = \text{RCH}(\text{NHR})\text{CN}$ , with acid sulfitcs,  $\text{RCH}=\text{NR} + \text{NaHSO}_3 = \text{RCH}(\text{NHR})\text{SO}_2\text{ONa}$ , with alcohols and phenols to form mixed aquo-ammono acetals,  $\text{RCH}=\text{NR} + \text{ROH} = \text{RCH}(\text{NHR})\text{OR}$ , and with primary and secondary amines to form ammono acetals,  $\text{RCH}=\text{NR} + \text{RNH}_2 = \text{RCH}(\text{NHR})_2$  and  $\text{RCH}=\text{NR} + \text{R}_2\text{NH} = \text{RCH}(\text{NHR})\text{NR}_2$ . They react with hydroxylamine,  $\text{RCH}=\text{NR} + \text{H}_2\text{N}:\text{OH} = \text{RCH}(\text{NHR})\text{NH}:\text{OH} \xrightarrow{-\text{RNH}_2} \text{RCH}=\text{N}:\text{OH}$ , with phenylhydrazine,  $\text{RCH}=\text{NR} + \text{C}_6\text{H}_5\text{NH}:\text{NH}_2 = \text{RCH}=\text{N}:\text{NHC}_6\text{H}_5 + \text{RNH}_2$ , and with Grignard reagents,  $\text{RCH}=\text{NR} + \text{RMgBr} = \text{R}_2\text{CH}=\text{N}(\text{MgBr})\text{R}$ . Finally certain Schiff bases have been observed to undergo aldol condensations, benzoin condensations and Cannizzaro reactions. It will be recognized that all the reactions thus summarized are just those which characterize the ordinary aquo aldehydes.

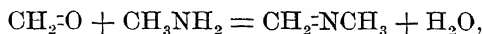
Since it would be obviously out of place to enter here upon an extended review of the large number of compounds included under the general designation of Schiff's bases, we shall content ourselves with a somewhat detailed discussion of a few representative com-

<sup>30</sup> Hinsberg and Koller, *Ber.*, 29, 1499 (1896).

<sup>31</sup> Schiff bases of the formulas,  $\text{RCH}=\text{N}(\text{RCO})$ ,  $\text{R}_2\text{C}=\text{N}(\text{RCO})$  and  $\text{RCH}=\text{N}(\text{RCNH})$ , are also known.

pounds in order to supply specific examples of the above general statements.

**Methylenemethylimine**,  $\text{CH}_2=\text{NCH}_3$ . Methylamine acts on formaldehyde in accordance with the equation,



to form an ammono aldehyde-ether which immediately polymerizes to the trimeric form.<sup>32</sup> When volatilized the trimer apparently dissociates into the monomolecular form. Further than this but little is known of the properties of this compound.

**Methylenediphenyldiamine**,  $\text{CH}_2(\text{NHC}_6\text{H}_5)_2$ , and **Anhydroformaldehydaniline**,  $(\text{CH}_2=\text{NC}_6\text{H}_5)_3$ . Formaldehyde reacts with two molecules of aniline to form methylenediphenyldiamine as represented by the equation,  $\text{CH}_2=\text{O} + 2\text{C}_6\text{H}_5\text{NH}_2 = \text{CH}_2(\text{NHC}_6\text{H}_5)_2 + \text{H}_2\text{O}$ .<sup>33</sup> Containing two imino hydrogen atoms methylenediphenyldiamine, like methylenediamine and methyleneglycol, is unstable. It readily loses aniline and passes over into methylenephenylyimine which in turn polymerizes to the trimolecular form known as anhydroformaldehydaniline,



just as formaldehyde and acetaldehyde polymerize to trioxymethylene and paraldehyde respectively and as methylene nitride dimerizes to hexamethylenetetramine.

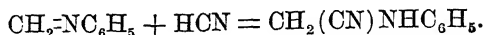
v. Miller and Plöchl<sup>34</sup> have shown that anhydroformaldehydaniline, which, acting as monomolecular methylenephenylyimine, shows characteristic aldehydic behavior as follows. First, it takes up aniline to form methylenediphenyldiamine in accordance with the equation,  $\text{CH}_2=\text{NC}_6\text{H}_5 + \text{C}_6\text{H}_5\text{NH}_2 = \text{CH}_2(\text{NHC}_6\text{H}_5)_2$ , which represents a reaction analogous to that involved in the formation of aldehyde ammonia by the action of ammonia on acetaldehyde. Second, it is hydrolyzed by the action of dilute acids to aquo formaldehyde and aniline,  $\text{CH}_2=\text{NC}_6\text{H}_5 + \text{H}_2\text{O} = \text{CH}_2=\text{O} + \text{C}_6\text{H}_5\text{NH}_2$ . Third, under the reducing action of zinc and hydrochloric acid, it is converted into methylaniline,  $\text{CH}_2=\text{NC}_6\text{H}_5 + \text{H}_2 = \text{CH}_3\text{NHC}_6\text{H}_5$ , a reaction which is analogous to the reduction of formaldehyde to methyl alcohol. Fourth, hydrocyanic acid acts on methylenephenylyimine, in a manner entirely analogous to its action on aquo formaldehyde, as represented by the equation,

<sup>32</sup> Gambier and Brochet, *Compt. rend.*, 120, 449 (1895); *Bull. soc. chim.*, [3] 13, 403 (1895).

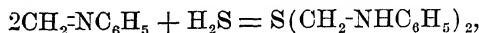
<sup>33</sup> Eberhardt and Welter, *Ber.*, 27, 1804 (1894); Bischoff, *Ber.*, 31, 3250 (1898); Eibner, *Ann. Chem.*, 302, 249 (1898).

<sup>34</sup> v. Miller and Plöchl, *Ber.*, 25, 2020 (1892).

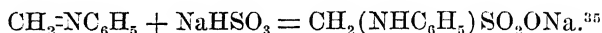




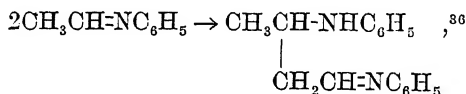
Fifth, with hydrogen sulfide anhydroformaldehydeaniline does not react to give thio formaldehyde and aniline, or the addition compound,  $\text{CH}_2(\text{SH})\text{NHC}_6\text{H}_5$ , as might be expected, but instead in accordance with the equation,



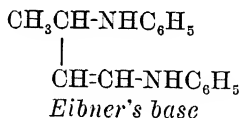
which still represents an aldehyde reaction in that it involves the direct addition of hydrogen sulfide. Finally, anhydroformaldehydeaniline has been observed to react with acid sodium sulfite to form an addition product as represented by the equation,



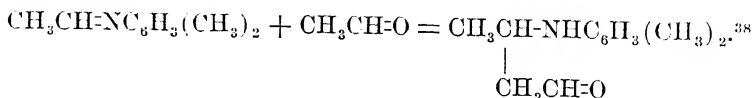
Ethylidenephénylimine,  $\text{CH}_3\text{CH-NC}_6\text{H}_5$ . 1. This aldehyde-ether differs from methylenephénylimine in that it tends to undergo aldol condensation rather than to polymerize as the latter does. Two molecules react with each other in accordance with the equation,



which obviously represents a typical aldol condensation. According to Eibner<sup>37</sup> this compound has the constitution represented by the formula,



2. Aldol condensations may also take place between Schiff bases and aquo aldehydes. For example, ethylidenexylylimine and acet-aldehyde have been observed to interact in accordance with the equation,



<sup>35</sup> Eibner, *Ann. Chem.*, **316**, 126 (1901).

<sup>36</sup> v. Miller and Plöchl, *Ber.*, **25**, 2029 (1892).

<sup>37</sup> Eibner, *Ann. Chem.*, **318**, 58 (1901).

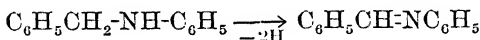
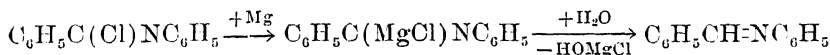
<sup>38</sup> v. Miller and Plöchl, *Ber.*, **29**, 1462, 1469 (1896).

3. Ethylidenephénylimine reacts with sulfurous acid as represented by the equation,



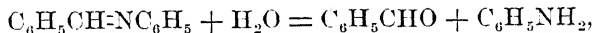
**Benzylidenephénylimine, Benzalaniline, Benzaldehydeanil,**  $\text{C}_6\text{H}_5\text{CH}=\text{NC}_6\text{H}_5$ . Our assumption that this compound is an ammono benzaldehyde-ether is supported by a wealth of observations some of which are summarized herewith.<sup>40</sup>

*Preparation.* Benzylidenephénylimine has been prepared by the action of aniline on benzaldehyde, on benzylideneimine and on hydrobenzamide. It has furthermore been obtained by the reducing action of metallic magnesium on phenylbenzimidochloride and by the oxidizing action of potassium permanganate on phenylbenzylamine. The equations,



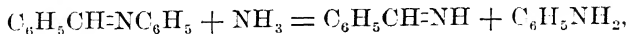
represent respectively the reduction of a derivative of benzoic acid to a derivative of benzaldehyde and the augmentation of a benzyl alcohol group to a benzaldehyde group.

*Hydrolysis.* Benzylidenephénylimine is hydrolyzed by the action of dilute acids to benzaldehyde and aniline,



which is to say that an ammono benzaldehyde-ether is hydrolyzed to aquo benzaldehyde and an ammono alcohol (ammono phenol).

*Ammonolysis.* Strain<sup>41</sup> has shown that benzylidenephénylimine is converted practically completely into amarine and aniline when allowed to stand in solution with ammonium chloride in liquid ammonia. The reactions involved take place in two steps, the first consisting in the ammonolysis of the aldehyde-ether,



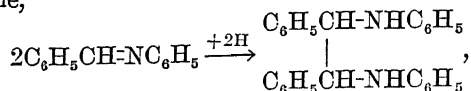
the second in the benzoin condensation of the benzylideneimine thus formed to amarine (p. 44).

<sup>39</sup> Eibner, *Ann. Chem.*, **316**, 121 (1901).

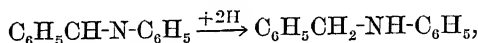
<sup>40</sup> Cf. Beilstein, "Handb. org. Chem.," 4th Ed., **12**, 198 (1929).

<sup>41</sup> Strain, *J. Am. Chem. Soc.*, **50**, 2218 (1928); Thesis, Stanford University (1927).

*Reduction.* Benzylidenephénylimine has been reduced to hydrobenzoinanilide,

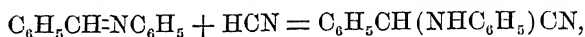


and also to phenylbenzylamine,

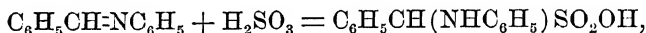


after the manner of the reduction of aquo benzaldehyde to hydrobenzoin and to benzyl alcohol.

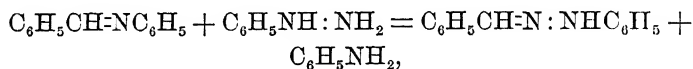
*Addition Products.* Benzylidenephénylimine forms addition products with hydrocyanic acid,



with sulfurous acid,



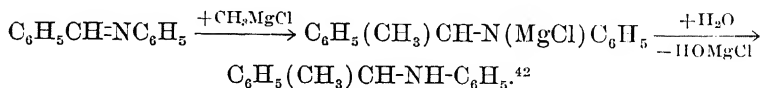
with acid sodium sulfite, and reacts with phenylhydrazine,



after the manner of the action of the respective reagents on aquo benzaldehyde.

*Action of Malonic Acid.* Malonic acid acts on benzylidenephénylimine to form cinnamic acid closely after the manner of its action on aquo benzaldehyde and on hydrobenzamide (p. 246).

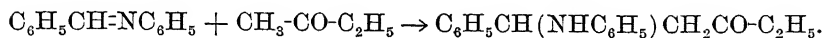
*Grignard Reactions.* Methylmagnesium chloride forms an addition product with benzylidenephénylimine, which on hydrolysis yields a secondary ammono alcohol,



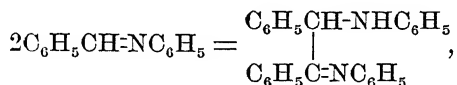
Closely similar reactions are involved in the formation of diphenylcarbinol from aquo benzaldehyde and of benzhydrylamine from hydrobenzamide (p. 250).

<sup>42</sup> This compound is an ammono secondary alcohol and at the same time an ammono phenol.

*Aldol Condensations.* With certain aquo ketones benzylidene-phenylimine undergoes the aldol condensation, with methylethyl-ketone, for example, as represented by the equation,

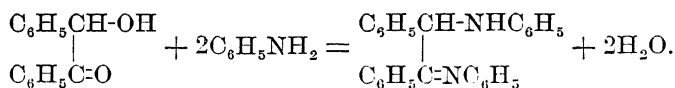


*Benzoin Condensation.* Strain has shown that when benzylidene-phenylimine is digested in liquid ammonia solution with potassium cyanide it undergoes a benzoin condensation,



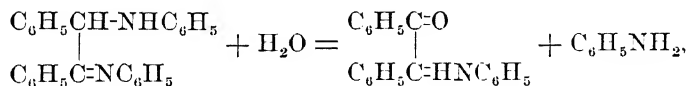
to form a compound known as benzoinanililide. Benzylidene-p-tolylimine undergoes condensation in a similar manner.

Benzoinanililide, which is a diphenyl derivative of an unknown ammono benzoin, was first prepared by Lachowicz<sup>43</sup> by heating a mixture of aniline hydrochloride and benzoin. The reaction involved is represented by the equation,

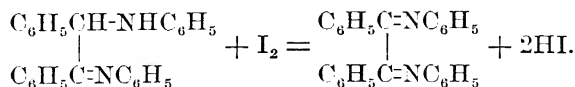


Aquo benzoin is converted, in principle ammonolyzed, to a diphenyl derivative of its nitrogen analog.

Strain found that benzoinanililide is hydrolyzed to benzoinaniline,



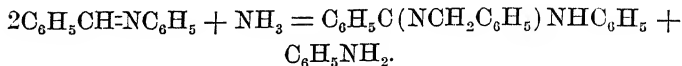
when heated with alcoholic hydrochloric acid and that, in liquid ammonia solution, it is nitridized by the action of iodine to benzil-dianil,



*Cannizzaro Reactions.* When benzylidenephénylimine and potassium amide are brought together in liquid ammonia solution N-

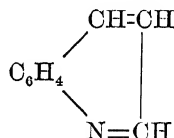
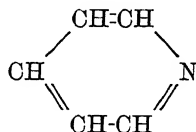
<sup>43</sup> Lachowicz, *Monatsh.*, 14, 281 (1893).

benzyl-N'-phenylbenzamidine and aniline are formed as represented by the equation,



Without going into details of the reactions concerned, which have been discussed by Strain, it is clear that the formation of the phenyl benzyl ester of an ammono benzoic acid involves a Cannizzaro reaction in that a benzyldene group of the one molecule of benzyldenephenylimine undergoes reduction to a benzyl group while simultaneously the benzyldene group of the second molecule of the aldehyde-ether is augmented to a benzoic acid group. Under similar conditions Strain converted benzyldene-p-tolylimine into benzyl-p-tolylbenzamidine and p-toluidine.

**Cyclic Aldehyde-Ethers and Cyclic Ketone-Ethers.** Since pyridine and quinoline when represented by the formulas,



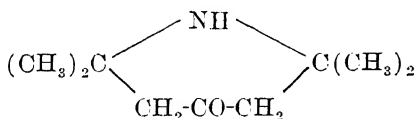
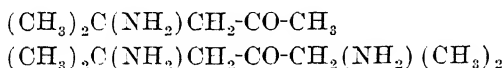
contain the group  $\text{RCH}=\text{NR}'$  it might be expected that they would be found to show aldehydic properties. Similarly the presence of the group,  $\text{RR}'\text{C}=\text{NR}''$ , in 2-methylpyridine and in 2-methylquinoline should lend to these compounds some of the characteristics of the ketones. That such is the case has been shown by Bergstrom and his coworkers.<sup>44</sup>

<sup>44</sup> Bergstrom and McAllister, *J. Am. Chem. Soc.*, **52**, 2845 (1930); Ogg and Bergstrom, *J. Am. Chem. Soc.*, **53**, 1846 (1931); Bergstrom, *J. Am. Chem. Soc.*, **53**, 245, 3027 (1931).

## CHAPTER XXVII.

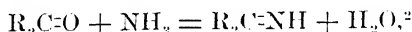
### KETONE-ALCOHOLS AND KETONE-ETHERS.

In view of the behavior of formaldehyde and acetaldehyde toward ammonia one might expect to find some one or more of the compounds represented by the formulas,  $(\text{CH}_3)_2\text{C}(\text{NH}_2)\text{OH}$ ,  $(\text{CH}_3)_2\text{C}(\text{NH}_2)_2$ ,  $(\text{CH}_3)_2\text{C}=\text{NH}$ ,  $[(\text{CH}_3)_2\text{C}=\text{NH}]_3$ ,  $[(\text{CH}_3)_2\text{C}]_3\text{N}_2$  and  $[(\text{CH}_3)_2\text{C}]_6\text{N}_4$ , among the products of the action of ammonia on acetone. Apparently, however, none of these compounds has been so prepared.<sup>1</sup> Three definitely characterized compounds, namely, diacetoneamine, triacetonediamine and triacetoneimine represented by the respective formulas,

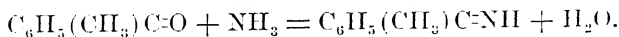


have been obtained by the action of ammonia on acetone. For the present purposes it will suffice to note that these compounds are aldol condensation products derived from acetone.

**Ammono Ketone-Alcohols,  $\text{R}_2\text{C}=\text{NH}$ .** *Formation.* Proceeding on the surmise that it might be possible to ammonolyze aquo ketones to ammono ketone-alcohols as represented by the equation,



Strain<sup>3</sup> heated acetophenone in liquid ammonia solution with the result that a small amount of acetophenoneimine was obtained.



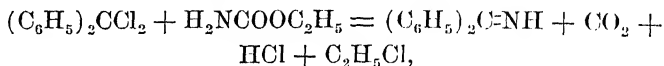
<sup>1</sup> Experimental observations reported by Thomae [*Arch. Pharm.*, **243**, 291, 294, 393 and 395 (1905); **244**, 643 and 653 (1906)] to the effect that a considerable number of ketones are acted upon by ammonia in accordance with the equation,  $3\text{R}_2\text{CO} + 2\text{NH}_3 = (\text{R}_2\text{C})_3\text{N}_2 + 3\text{H}_2\text{O}$ , have been severely criticized by W. Traube [*Arch. Pharm.*, **246**, 666 (1909) and *Ber.*, **42**, 3298 (1909) 1].

<sup>2</sup> It is known that the ketimines are easily hydrolyzed to ketones and ammonia as represented by the above equation read from right to left.

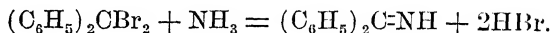
<sup>3</sup> Strain, *J. Am. Chem. Soc.*, **52**, 820 (1930).

When the solution of acetophenone was heated in the presence of ammonobasic aluminum chloride, which acts as an efficient water absorbent, the yield was increased to thirty per cent. By treating benzophenone in a similar manner Strain obtained good yields of benzophenoneimine,  $(C_6H_5)_2C=NH$ .

Benzophenoneimine has also been prepared by heating benzophenone chloride with urethane,<sup>4</sup> and by the action of ammonia on benzophenone bromide.<sup>5</sup> In the one case urethane may be said to function as an ammonolyzing agent,

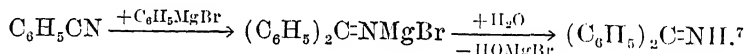


in the other the ketone-bromide is ammonolyzed to a ketone-alcohol by the action of ammonia,



Mignonac<sup>6</sup> obtained ketimines in moderate yields by passing ketone vapors mixed with ammonia over thoria heated to temperatures of 300° to 400°. Benzophenone, for example, has thus been ammonolyzed to benzophenoneimine and water as represented by the equation,  $(C_6H_5)_2C=O + NH_3 = (C_6H_5)_2C=NH + H_2O$ .

Several aromatic and mixed aliphatic aromatic ketimines have been prepared by carefully hydrolyzing the products of the action of Grignard reagents on nitriles, benzophenoneimine for instance, in accordance with the scheme,



An acid anammonide is thereby converted into an ammono ketone-alcohol in a manner closely resembling the reduction of acetic anhydride to methylethylketone by way of the zinc ethyl addition product.<sup>8</sup>

Cornell<sup>9</sup> obtained benzophenoneimine by treating Moureu and Mignonac's benzonitrile phenylmagnesium bromide addition product with liquid ammonia thereby obtaining benzophenoneimine in a medium free from water.

Cornell's observations have been confirmed by Smith<sup>10</sup> who has

<sup>4</sup> Hantzsch and Kraft, *Ber.*, **24**, 3516 (1891).

<sup>5</sup> Moore, *Ber.*, **43**, 564 (1910).

<sup>6</sup> Mignonac, *Compt. rend.*, **169**, 237 (1919).

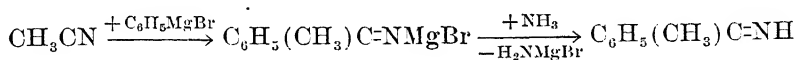
<sup>7</sup> Moureu and Mignonac, *Ann. Chim.*, [9] **14**, 326 (1920).

<sup>8</sup> Granichstädten and Werner, *Monatsh.*, **22**, 316 (1901).

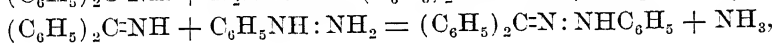
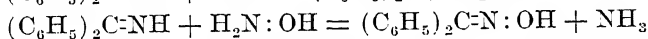
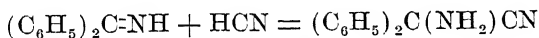
<sup>9</sup> Cornell, Thesis, Stanford University (1926).

<sup>10</sup> G. E. P. Smith, Jr., Thesis, Stanford University (1930).

shown also that acetophenoneimine is obtained in fair yield when the product of the action of phenylmagnesium bromide on acetonitrile is treated with liquid ammonia. The reactions here involved are represented by the scheme,

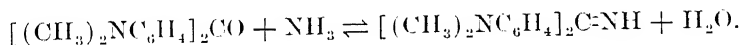


*Reactions.* Little is known of the chemical behavior of the simpler ketimines other than that they are hydrolyzed with the greatest ease to aquo ketones and ammonia and that a few of them have been found to react with hydrocyanic acid to form cyanamines, with hydroxylamine to form ketone oximes and with phenylhydrazine to form phenylhydrazones. Smith<sup>10a</sup> has shown that benzophenoneimine for example reacts with these reagents as represented by the respective equations,



to form respectively a ketone cyanamine, a ketone oxime and a ketone phenylhydrazone.

*Auramine.* A somewhat more complicated ketimine which shows the properties of an ammono ketone-alcohol is the familiar dyestuff known as auramine or tetramethyldiaminobenzophenoneimine. This compound is formed by the action of ammonia (ammonium chloride in the presence of zinc chloride), on Michler's ketone and, inversely, is hydrolyzed to the latter by the action of dilute acids as represented by the reversible equation,<sup>11</sup>



According to Fehrmann auramine reacts with hydrogen sulfide to form the thio ketone,  $[(\text{CH}_3)_2\text{NC}_6\text{H}_4]_2\text{CS}$ , and on treatment with aniline is converted into the ammono ketone-ether  $[(\text{CH}_3)_2\text{NC}_6\text{H}_4]_2\text{C}=\text{NC}_6\text{H}_5$ . Furthermore, auramine forms an addition product with hydrogen cyanide,  $[(\text{CH}_3)_2\text{NC}_6\text{H}_4]_2\text{C}(\text{NH}_2)\text{CN}$ ,<sup>12</sup> and is reduced to leucauramine,  $[(\text{CH}_3)_2\text{C}_6\text{H}_4]_2\text{CHNH}_2$ , which is a secondary ammono alcohol.

*Ammono Ketone-Ethers.*  $\text{R}_2\text{CH}=\text{NR}$ . Among the known compounds of this general formula are isopropylidenephnylimine, iso-

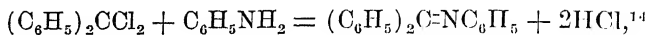
<sup>10a</sup> G. E. P. Smith, Jr., Thesis, Stanford University (1930).

<sup>11</sup> Fehrmann, *Ber.*, 20, 2847 (1887).

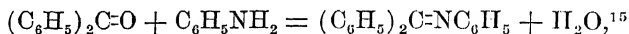
<sup>12</sup> Albrecht, *Ber.*, 27, 3294 (1894).



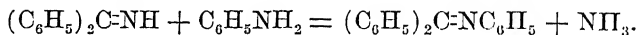
lated from the mixture resulting from the action of aniline on acetone,  $(\text{CH}_3)_2\text{C}=\text{O} + \text{C}_6\text{H}_5\text{NH}_2 = (\text{CH}_3)_2\text{C}=\text{NC}_6\text{H}_5 + \text{H}_2\text{O}$ ,<sup>13</sup> and benzophenonephenylimine, which has been prepared by the action of aniline on benzophenonedichloride,



on benzophenone,

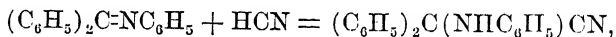


and on benzophenoneimine,

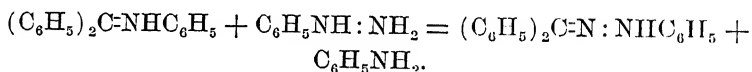


Another ketone-ether, known as benzylacetophenoneimine, is formed by the action of benzylamine on acetophenone.<sup>16</sup>

All these ammono ketone-ethers are readily hydrolyzed by the action of dilute acids to the respective aquo ketones and amines. Benzophenonephenylimine has been observed to form an addition product with hydrocyanic acid,<sup>17</sup>



and to react with phenylhydrazine to form benzophenonephenylhydrazone and aniline,<sup>18</sup>



It is interesting to add that ammono ketone esters of the type represented by the formula,  $(\text{C}_6\text{H}_5)_2\text{C}=\text{NCOCH}_3$ , have been prepared. This compound readily hydrolyzes to benzophenone acetic acid and ammonia.

<sup>13</sup> Riehm, *Ann. Chem.*, **238**, 10 (1887).

<sup>14</sup> Pauly, *Ann. Chem.*, **187**, 199 (1877).

<sup>15</sup> Nägeli, *Bull. soc. chim.*, [2] **21**, 785 (1899); Graebe, *Ber.*, **32**, 1680 (1899).

<sup>16</sup> Hantzsch and v. Hornbostel, *Ber.*, **30**, 3007 (1897).

<sup>17</sup> v. Miller, Plöchl and Rohde, *Ber.*, **25**, 2056 (1892).

<sup>18</sup> Ott, *Monatsh.*, **26**, 347 (1905).

<sup>19</sup> Moureu and Mignonac, *Ann. Chim.*, [9] **14**, 340 (1920).

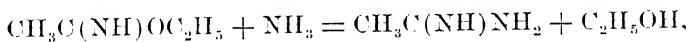
## CHAPTER XXVIII.

### CARBAZYLIC ACIDS.

**Acid Amidines.** Just as the scheme,  $\text{CH}_3\text{C}(\text{OH})_3 \rightarrow \text{CH}_3\text{COOH} \rightarrow (\text{CH}_3\text{CO})_2\text{O}$ , is sometimes used to show the relations between ortho acetic acid, ordinary acetic acid and acetic anhydride, so one may write the analogous scheme,  $\text{CH}_3\text{C}(\text{NH}_2)_3 \rightarrow \text{CH}_3\text{C}(\text{NH})\text{NH}_2 \rightarrow \text{CH}_3\text{CN}$ , to represent the deammonation of an hypothetical ortho ammono acetic acid successively to acetamidine and methyl cyanide. These two compounds thus appear as the nitrogen analogs of ordinary acetic acid and acetic anhydride respectively and as such are to be regarded, the one as an ammono acetic acid, the other as an acetic acid anammonide. Formamidine,  $\text{HC}(\text{NH})\text{NH}_2$ , is an ammono formic acid, benzamidine,  $\text{C}_6\text{H}_5\text{C}(\text{NH})\text{NH}_2$ , is an ammono benzoic acid while the acid amidines in general as nitrogen analogs of the carboxylic acids may be fittingly called carbazyllic acids.

The methods of preparation and the general behavior of the acid amidines support the formal relations indicated above to the effect that they are, so to speak, the carboxylic acids of the nitrogen system.

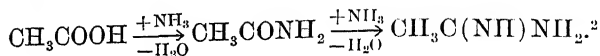
*Formation.* 1. Pinner<sup>1</sup> first prepared acid amidines by the action of alcoholic ammonia on imidoester hydrochlorides. Acetamidine, for example, is formed by the action of ammonia on acetimidoethyl ester hydrochloride as represented by the equation.



in accordance with which an O-ester of an aquo-ammono acetic acid is ammonolyzed to an ammono acetic acid and aquo ethyl alcohol.

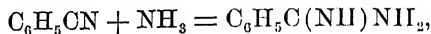
2. Looking upon acetamidine as the nitrogen analog of acetic acid it should be possible to convert the latter into the former by the ammonolytic action of ammonia. Accordingly it has been found that acetamidine hydrochloride is formed when a liquid ammonia solution of ammonium acetate and ammonium chloride is heated for a time at a temperature of  $90^\circ$  to  $100^\circ$ . The reaction involved consists in the ammonolysis of aquo acetic acid to an ammono acetic acid as represented by the equation,

<sup>1</sup> Pinner, "Die Imidoäther und ihre Derivate," Berlin, 1892.



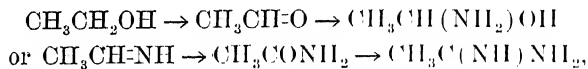
Antedating the observations of Chuck, Fichter<sup>3</sup> found that acetamidine nitrate is formed when a liquid ammonia solution containing acetamide and ammonium nitrate is heated at 170°.

3. Under ordinary conditions the nitriles do not unite with ammonia to form amidines as they might be expected to do on the assumption that they are acid anammonides. It happens however that the expected reactions take place when nitriles are heated with ammonium chloride in liquid ammonia solution. Cornell<sup>4</sup> found that propionitrile and benzonitrile when so treated are partly converted respectively into propionamidine and benzamidine. The formation of benzamidine from benzonitrile,



may be said to consist in the ammonation of benzoic anammonide to ammono benzoic acid.

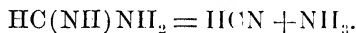
4. Acetamidine nitrate is among the products formed at the anode when a saturated solution of ammonium carbonate containing a relatively small amount of ethyl alcohol is subjected to electrolysis.<sup>5</sup> Fichter represents the reactions involved as follows,



in accordance with which it may be said that first and last aqueous ethyl alcohol is augmented to ammono acetic acid.

5. Fichter furthermore obtained acetamidine by the action of oxidizing agents, such as calcium permanganate and ammonium persulfate, on ethyl alcohol and on acetaldehyde in ammoniacal ammonium nitrate solution.

*Deammonation.* When formamidine hydrochloride is heated it breaks down to form hydrocyanic acid and ammonium chloride, which is to say that ammono formic acid undergoes deammonation to yield formic anammonide and ammonia,



Under similar treatment benzamidine yields benzonitrile, cyanophenene, which is trimolecular benzoic anammonide, and ammon

<sup>2</sup> Unpublished observations by Faw Yap Chuck.

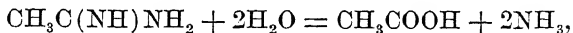
<sup>3</sup> Fichter, *Z. Elektrochem.*, **18**, 652 (1912).

<sup>4</sup> Cornell, *J. Am. Chem. Soc.*, **50**, 3317 (1928).

<sup>5</sup> Fichter, *Z. Elektrochem.*, **18**, 652 (1912).

Pinner<sup>6</sup> prepared an ammono dibenzoic acid of the formula,  $(C_6H_5CNH)_2NH$ , which he named dibenzenylimidoimide, by the deammonating action of acetic anhydride on benzamidine.

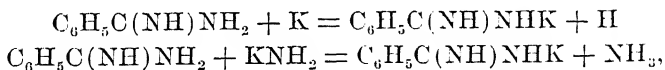
*Hydrolysis.* By the action of warm water acetamidine is converted into aquo acetic acid and ammonia,



while phenylacetamidine, under similar conditions yields phenylacetamide and ammonia. In the one case the ammono acid is hydrolyzed to the aquo acid, in the other the hydrolysis stops with the formation of the mixed aquo-ammono acid. At higher temperatures phenylacetamide is of course hydrolyzed to aquo phenylacetic acid and ammonia.

**Metallic Salts.** As acids the amidines are far too weak to show acid properties in water solution. Indeed they are generally spoken of as strong bases, though they are bases only in the sense that they unite with acids as ammonia does to form salts and that in solution in water they show an alkaline reaction.

Investigations conducted in this laboratory have shown that in liquid ammonia the acid properties of the amidines are clearly in evidence to the extent at least that they react with the alkali metals and their amides to form metallic derivatives. Benzamidine, for example, reacts with metallic potassium and with potassium amide in accordance with the respective equations,



to form monopotassium ammonobenzoate.

Metallic salts of the amidines are also formed when nitriles, which are carbylic acid anammonides, and metallic amides are brought together in liquid ammonia solution. Just as acetic anhydride acts on potassium hydroxide to form potassium acetate, so acetonitrile reacts with potassium amide in accordance with the equation,  $CH_3CN + KNH_2 = CH_3C(NH)NHK$ , to form a nitrogen analog of ordinary potassium acetate, namely, a potassium acetamidine.

Although formally acetamidine is a tribasic acid it has not been possible, even in the presence of a large excess of potassium amide, to replace more than one of the hydrogen atoms by metal. When, however, the stepwise retrogression of the acidity of the three hydrogen atoms in a fairly strong tribasic acid such as orthophos-

<sup>6</sup> Pinner, *Ber.*, 8, 11, 8 (1878).

phoric acid is recalled, it is not surprising to find such weak acids as the amidines functioning as monobasic acids.

Excepting as otherwise indicated the salts listed below have been prepared by the action of metallic amides on nitriles using liquid ammonia as a solvent. With the exceptions noted all these salts are soluble in liquid ammonia from which they separate well crystallized and of sharply definite composition. All undergo hydrolysis in the presence of water to form the respective acid amidines, metallic hydroxides and ammonia.<sup>7</sup>

*Potassium Ammonoacetate*,  $\text{CH}_3\text{C}(\text{NH})\text{NHK}$ , has been prepared by the direct addition of potassium amide to acetonitrile, as noted above and also by the action of potassium amide on acetamidine hydrochloride.

*Sodium Ammonoacetate*,  $\text{CH}_3\text{C}(\text{NH})\text{NHNa}$ .

*Potassium Ammonopropionate*,  $\text{CH}_3\text{CH}_2\text{C}(\text{NH})\text{NHK}$ .

*Sodium Ammonopropionate*,  $\text{CH}_3\text{CH}_2\text{C}(\text{NH})\text{NHNa}$ .

*Calcium Ammonopropionate*,  $[\text{C}_2\text{H}_5\text{C}(\text{NH})\text{NH}]_2\text{Ca}$ . This salt was obtained in the form of a microcrystalline powder by the action of a liquid ammonia solution of propionitrile on the practically insoluble calcium amide. The specimen analyzed contained a considerable admixture of unchanged calcium amide.

*Potassium Ammono-n-butyrate*,  $\text{C}_3\text{H}_7\text{C}(\text{NH})\text{NHK}$ .

*Sodium Ammono-n-butyrate*,  $\text{C}_3\text{H}_7\text{C}(\text{NH})\text{NHNa}$ .

*Potassium Ammono-n-valerate*,  $\text{C}_4\text{H}_9\text{C}(\text{NH})\text{NHK}$ .

*Potassium Ammono-iso-caproate*,  $\text{C}_5\text{H}_{11}\text{C}(\text{NH})\text{NHK}$ .

*Potassium Ammonopalmitate*,  $\text{C}_{15}\text{H}_{31}\text{C}(\text{NH})\text{NHK}$ , separates as a bulky, amorphous precipitate when the nitrile of palmitic acid and potassium amide are brought together in liquid ammonia solution.

*Potassium Ammonophenylacetate*,  $\text{C}_6\text{H}_5\text{CH}_2\text{C}(\text{NH})\text{NHK}$ .

*Potassium Ammono-p-tolylacetate*,  $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{C}(\text{NH})\text{NHK}$ .

*Dipotassium Ammonosuccinate*,  $\text{KHN}(\text{NH})\text{C}-\text{CH}_2-\text{CH}_2-\text{C}(\text{NH})-\text{NHK}$ , appears as an insoluble precipitate when succinonitrile and potassium amide are brought together in liquid ammonia solution.

*Potassium Ammonobenzoate*,  $\text{C}_6\text{H}_5\text{C}(\text{NH})\text{NHK}$ , has been prepared by the action of benzamidine on metallic potassium and on potassium amide, and also by the action of benzonitrile on potassium amide.

*Sodium Ammonobenzoate*,  $\text{C}_6\text{H}_5\text{C}(\text{NH})\text{NHNa}$ .

*Calcium Ammonobenzoate*,  $[\text{C}_6\text{H}_5\text{C}(\text{NH})\text{NH}]_2\text{Ca}$ , has been obtained as an insoluble microcrystalline powder by digesting calcium amide with a liquid ammonia solution of benzonitrile.

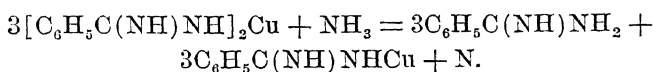
*Silver Ammonobenzoate*,  $\text{C}_6\text{H}_5\text{C}(\text{NH})\text{NHAg}$ , separates as a precipitate when silver nitrate and potassium benzamidine are brought

<sup>7</sup> Benedict, Thesis, Stanford University (1924); Cornell, *J. Am. Chem. Soc.* 50, 3311 (1928).

together in liquid ammonia solution. The same salt is formed as a precipitate when sodium hydroxide is added to a water solution containing benzanidine and silver nitrate.<sup>8</sup>

*Cupric Ammonobenzoate*,  $[\text{C}_6\text{H}_5\text{C}(\text{NH})\text{NH}]_2\text{Cu}$ , is formed as a green precipitate when potassium benzanidine and cupric nitrate are brought together in liquid ammonia solution.

*Cuprous Ammonobenzoate*,  $\text{C}_6\text{H}_5\text{C}(\text{NH})\text{NHCu}$ . In alkaline solution, that is to say in the presence of a small amount of potassium amide, the green cupric ammonobenzoate is converted into the colorless, insoluble cuprous salt. Cupric copper is reduced to the cuprous state, while simultaneously ammonia is augmented to nitrogen. The reactions over all may be represented by the equation,



*Potassium Ammono-p-toluate*,  $\text{CH}_3\text{C}_6\text{H}_4\text{C}(\text{NH})\text{NHK}$ .

*Potassium Ammonodibenzoate (Pyrobenzoate)*,  $(\text{C}_6\text{H}_5\text{CNH})_2\text{NK}$ . This potassium salt of Pinner's dibenzoylimidoimide<sup>9</sup> has been obtained by dissolving the acid, which is practically insoluble in liquid ammonia, in a solution of potassium amide. The salt is very soluble.

*Sodium Ammonodibenzoate*,  $(\text{C}_6\text{H}_5\text{CNH})_2\text{NNa}$ . The insoluble acid and the slightly soluble sodium amide, in contact with liquid ammonia, pass rapidly into solution to form the moderately soluble sodium salt.

**Cyclic Carbazylic Acids.** Examples of cyclic carbazylic

acids are succinimidine,  $\begin{array}{c} \text{CH}_2-\text{C}(\text{NH}) \\ | \quad \diagdown \\ \text{CH}_2-\text{C}(\text{NH}) \quad \diagup \quad \text{NH} \end{array}$  and phthalimidine,

$\begin{array}{c} \text{C}(\text{NH}) \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \quad \text{NH} \\ \diagdown \quad \diagup \\ \text{C}(\text{NH}) \end{array}$ . Imidazol,  $\begin{array}{c} \text{CH}-\text{N} \\ || \quad \diagdown \\ \text{CH}-\text{NH} \end{array}$ , and benzimidazole,

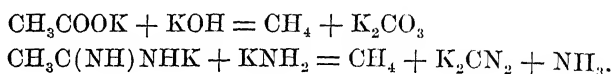
$\begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \quad \text{CH} \\ \diagdown \quad \diagup \\ \text{NH} \end{array}$ , are cyclic ammonoformates. Metallic salts of all

four of these compounds have been prepared.

<sup>8</sup> Pinner and Klein, *Ber.*, 11, 6 (1878).

<sup>9</sup> Pinner, *Ber.*, 11, 8 (1878).

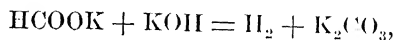
**Pyrogenetic Decomposition of Carbazylic Acid Salts.** If potassium acetamidine be looked upon as a potassium salt of an ammono acetic acid it follows that just as ordinary potassium acetate when heated with potassium hydroxide yields methane and potassium aquocarbonate so on heating a mixture of potassium ammono acetate and potassium amide one might expect to observe the formation of methane and a potassium ammonocarbonate. As a matter of fact this is just what happens. Methane and dipotassium cyanamide are formed. The parallel reactions, which may be said to involve the augmentation of carbylic acid carbon to carbonic acid carbon and the simultaneous reduction of methyl carbon to methane carbon, are represented by the equations,



The reaction thus represented is moreover a general one since Cornell<sup>10</sup> has found that the potassium salts of propionamidine, n-butyramidine, n-valeramidine, isocaproamidine and benzamidine when heated with potassium amide, react to form dipotassium cyanamide on the one hand and ethane, propane, butane, isopentane and benzene respectively on the other. Furthermore benzene and sodium cyanamide are obtained as represented by the equation  $\text{C}_6\text{H}_5\text{CN} + 2\text{NaNH}_2 = \text{C}_6\text{H}_6 + \text{Na}_2\text{CN}_2 + \text{NH}_3$ , when benzonitrile (benzoic anammonide) and sodium amide are heated together in a closed tube. It is reasonable to assume that a sodium salt of benzamidine is formed as a primary product.

Kirkish<sup>11</sup> has recently shown that phenylacetonitrile and p-toluenitrile when heated with sodium amide yield toluene and sodium cyanamide and that  $\beta$ -naphthonitrile yields naphthalene and sodium cyanamide. In each case nitrogen, hydrogen and other pyrogenic products are also formed.

Finally just as hydrogen and potassium carbonate are formed in accordance with the familiar equation,

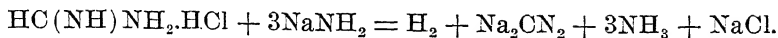


when a mixture of potassium formate and potassium hydroxide is heated, so heating a mixture of potassium formamidine and potassium amide should result in the formation of a potassium ammono carbonate and hydrogen. A potassium salt of ammono formic acid has not been made. However, when formamidine hydrochloride is

<sup>10</sup> Cornell, *J. Am. Chem. Soc.*, **50**, 3311 (1928).

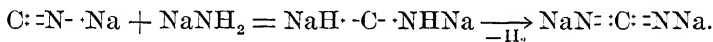
<sup>11</sup> Kirkish, Thesis, Stanford University, 1931.

heated with sodium amide, sodium cyanamide and hydrogen are formed as represented by the equation,



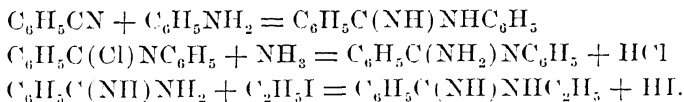
When formimido ethyl ester is similarly heated with excess of potassium amide, hydrogen gas and potassium cyanamide are among the products formed.<sup>12</sup>

The reactions involved in the conversion of formamidine into sodium cyanamide and hydrogen resemble closely those which take place when sodium cyanide and hydrogen are formed by the action of fused sodium amide on sodium cyanide. It is not unreasonable to assume that sodium amide acts on sodium cyanide to form a disodium ammonocarbonite which by intramolecular nitridation and reduction yields disodium ammonocarbonate and hydrogen,

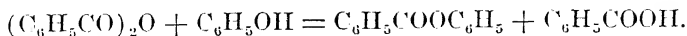


**Esters.** Regarding the acid amidines as ammono acids it follows that their alkyl and aryl derivatives are to be looked upon as carba-zylic acid esters. It will suffice present purposes to show that the methods of preparation and the ammonolytic and hydrolytic behavior of a limited number of representatives of the four classes of compounds represented by the formulas, (1)  $\text{RC}(\text{NH})\text{NHR}$ , (2)  $\text{RC}(\text{NR})\text{NHR}$ , (3)  $\text{RC}(\text{NH})\text{NR}_2$ , and  $\text{RC}(\text{NR})\text{NR}_2$ , are in harmony with this view.

(1)  $\text{RC}(\text{NH})\text{NHR}$ . Three methods for the preparation of members of the first class of compounds are represented by the equations,



In accordance with the first equation a phenyl ammonobenzoate is formed by the action of an ammono alcohol (ammono phenol) on benzoic anammonide in a manner closely resembling the formation of phenyl aquobenzoate and aquo benzoic acid by the action of phenol on benzoic anhydride,



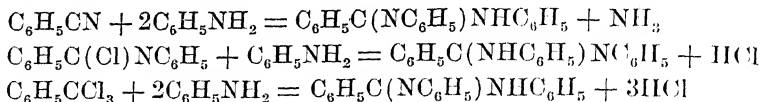
In the one case an acid ester is formed, in the other a neutral ester and the free acid. The reaction represented by the second equation

<sup>12</sup> Unpublished observations.



is of a familiar sort in that it involves the ammonolytic replacement of chlorine in a benzoic acid chloride by an amido group. The third equation recalls the formation of ethyl aquobenzoate by the action of ethyl iodide on sodium aquobenzoate.

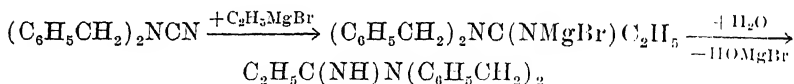
(2)  $RC(NR)NHR$ . N-N'-Diphenylbenzamidine has been prepared by the action of aniline on benzonitrile, on benzanilide imide-chloride and on benzoetrichloride as represented by the equations,



in accordance with which a diphenyl ammonobenzoate is formed by the action of aniline first, on benzoic anammonide, second, on a benzoic acid ester-chloride and third, on a benzoic acid chloride.

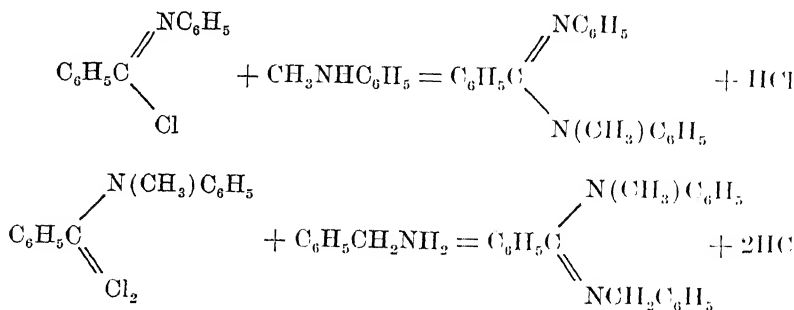
$RC(NH)NR_2$ . N-N-Diphenyl ammonobenzoate is formed when benzoic anammonide is heated with diphenylamine hydrochloride,  $\text{C}_6\text{H}_5\text{CN} + \text{HN}(\text{C}_6\text{H}_5)_2 = \text{C}_6\text{H}_5\text{C}(\text{NH})\text{N}(\text{C}_6\text{H}_5)_2$ .

N-N-dibenzyl ammonopropionate has been prepared by hydrolyzing the product of the action of ethylmagnesium bromide on dibenzylecyanamide.<sup>13</sup> The reactions involved, which are represented by the scheme,

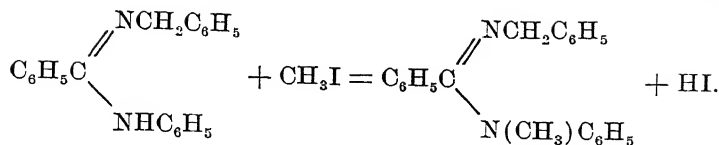


bring about the reduction of an ammono carbonic acid ester to an ester of a carbazylic acid.

(4)  $RC(NR)NR_2$ . Examples of three methods for the preparation of neutral esters of benzamidine are represented by the equations,

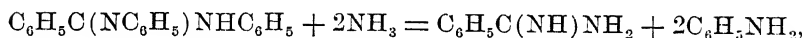


<sup>13</sup> Adams and Beebe, *J. Am. Chem. Soc.*, **38**, 2268 (1906).



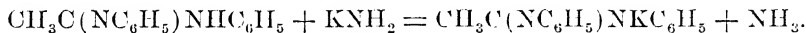
In accordance with the first two equations neutral ammono benzoates are formed by the action of ammono alcohols on benzoic acid ester-chlorides. The third equation is of a familiar sort in that it involves the substitution of an acid hydrogen atom by an alkyl group.<sup>14</sup>

*Ammonolysis.* Just as ordinary esters are familiarly known to undergo hydrolytic decomposition, slowly by the action of water alone, much more rapidly in the presence of acid or alkali; so we should expect to find esters of the carbazyllic acids ready to undergo ammonolytic decomposition when treated with ammonia alone or with solutions of acids or of alkali amides in this solvent. The ammonolytic behavior of but two such esters has so far been studied. When N-N'-diphenylbenzamidine is heated with ammonium chloride in liquid ammonia solution it is ammonolyzed in accordance with the equation,



to benzamidine and aniline. Treated in a similar manner N-N'-diphenyl ammonoacetate,  $\text{CH}_3\text{C}(\text{NC}_6\text{H}_5)\text{NHC}_6\text{H}_5$ , has been ammonolyzed to acetamidine and aniline.<sup>15</sup>

**Ester-Salts.** Derivatives of the acid amidines represented by the general formulas,  $\text{RC}(\text{NH})\text{NHR}$ ,  $\text{RC}(\text{NH})\text{NR}_2$  and  $\text{RC}(\text{NR})\text{NHR}$ , are formally acid esters and as such should be capable of forming metallic salts. Two such compounds are known. A silver salt,  $\text{C}_{14}\text{H}_{13}\text{N}_2\text{Ag}$ ,<sup>16</sup> and a potassium salt,  $\text{C}_{14}\text{H}_{13}\text{N}_2\text{K}$ , of N-N'-diphenylacetamidine<sup>17</sup> have been prepared, the latter by the action of potassium amide on the acid ester in liquid ammonia solution,



<sup>14</sup> J. v. Braun, *Ber.*, 37, 2678 (1904); Beckmann and Fellrath, *Ann. Chem.*, 273, 5 (1893).

<sup>15</sup> Niemann, Thesis, Stanford University, 1926.

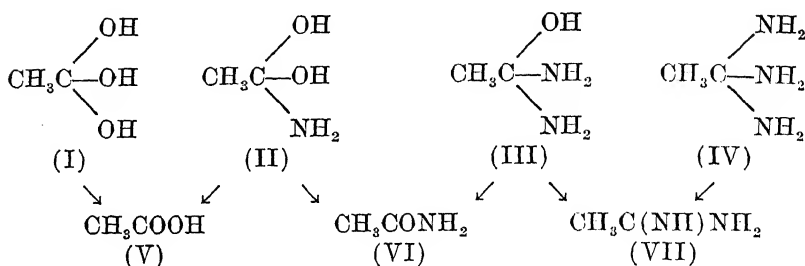
<sup>16</sup> Bamberger and Lorenzen, *Ann. Chem.*, 273, 300 (1893).

<sup>17</sup> Unpublished observations.

## CHAPTER XXIX.

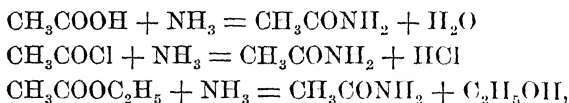
### CARBOXAZYLIC ACIDS.

**Acid Amides.** The close relationship existing between acetic acid, acetamide and acetamidine may be shown by means of the scheme,



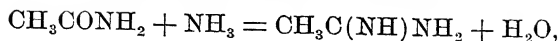
which represents four hypothetical ortho acetic acids, an aquo acid (I), an ammono acid (IV) and two aquo-ammono acids (II) and (III), as undergoing desolvation to form three known acetic acids, namely ordinary aquo acetic acid (V), an ammono acetic acid (VII) and an aquo-ammono acetic acid (VI). Acids represented by the general formula,  $\text{RCOOH}$ , are known as carboxylic acids, we have chosen to call the acid amidines carbazylic acids, and shall find it convenient to speak of the acid amides as carboxazylic acids.

*Formation.* Three familiar processes for the preparation of acetamide, a typical carboxazylic acid, are summarized by the equations,



which represent the formation of aquo-ammono acetic acid by the ammonolytic action of ammonia on aquo acetic acid, on acetyl chloride and on ethyl aquo-acetate respectively.

*Hydrolysis and Ammonolysis.* Acetamide may be hydrolyzed to aquo acetic acid and ammonia as represented by the first of the above equations read from right to left. It is ammonolyzed in accordance with the equation,



to acetamidine when heated with ammonium chloride in liquid ammonia solution.<sup>1</sup>

When acetamide is heated in a current of hydrochloric acid gas acetic acid and acetamidine hydrochloride are formed as represented by the equation,



which is to say that the one molecule of acetamide ammonolyzes the second to acetamidine, the one at the same time undergoing hydrolysis to aquo acetic acid.

*Acid Properties.* Although metallic derivatives of the acid amides have long been known it is nevertheless true that acetamide and its homologs, benzamide and the other aromatic acid amides have apparently never been looked upon definitely as acids. They are in general neutral compounds the metallic derivatives of which (excepting the mercury and silver compounds) are hydrolyzed in the presence of water.<sup>2</sup>

In solution in liquid ammonia, however, their acid properties are unmistakable. In such solutions the acid amides react with the more electropositive metals and with metallic amides to form metallic salts and are distinct conductors of electricity.<sup>3</sup> The red color of a slightly alkaline liquid ammonia solution of phenolphthalein is discharged, not very sharply it is true, when acetamide is added to such a solution. Formamide, which is a distinctly stronger acid, discharges the color more sharply.

*Metallic Salts.* Contingent upon the circumstance that they are more or less resistant to the hydrolytic action of water the silver and mercury salts of most of the known acid amides and imides have been prepared. Acid amide salts of other metals, however, are less numerous known and this for the reason that as salts of very weak acids they are incapable of existence in the presence of water. Such salts have been prepared by various methods in which solvents other than water have been used. Liquid ammonia especially, by reason of its low solvolyzing power as compared with water together with its conspicuous power as a solvent, has proved itself an

<sup>1</sup> Unpublished observation.

<sup>1a</sup> Strecker, *Ann. Chem.*, **103**, 324 (1857).

<sup>2</sup> Branch and Clayton [*J. Am. Chem. Soc.*, **50**, 1680 (1928)] have given  $8 \times 10^{-10}$  and  $1 \times 10^{-14}$  to  $1 \times 10^{-15}$  as the dissociation constants in water of acetamide and benzamide respectively at 25°.

<sup>3</sup> Franklin and Kraus, *Am. Chem. J.*, **23**, 277 (1900); *J. Am. Chem. Soc.*, **27**, 191 (1905); Franklin, *Z. physik. Chem.*, **69**, 272 (1909).

excellent solvent in which to carry out the reactions with which we are here concerned.\*

The following named and formulated salts have been prepared by means of reactions carried out in liquid ammonia solution.

*Potassium Aquo-Ammono-Formate*,  $\text{HCONHK}$ . In the presence of excess of potassium amide the salt rapidly breaks down to form hydrogen and potassium cyanate.

*Sodium Aquo-Ammono-Formate*,  $\text{HCONHNa}$ , has been prepared by the action of formamide in liquid ammonia solution and in dry benzene on sodium amide and by the action of sodium ethylate on formamide in alcohol-ether solution.

*Potassium Aquo-Ammono-Acetate*,  $\text{CH}_3\text{CONHK}$ .

*Sodium Aquo-Ammono-Acetate*,  $\text{CH}_3\text{CONHNa}$ , has been prepared by the action of sodium ethylate on acetamide in alcohol solution and of sodium amide on acetamide in benzene solution and in liquid ammonia solution.

*Silver Aquo-Ammono-Acetate*,  $\text{CH}_3\text{CONHAg}$  and  $\text{CH}_3\text{CONHAg} \cdot 2\text{NH}_3$ . The ammonia-free salt has been obtained by dissolving silver oxide in a water solution of acetamide. The ammoniated salt crystallizes from a solution formed by dissolving silver amide or silver oxide in a liquid ammonia solution of acetamide.

*Magnesium Aquo-Ammono-Acetate*,  $(\text{CH}_3\text{CONH})_2\text{Mg} \cdot 4\text{NH}_3$ . This well-crystallized product, which is very slightly soluble in liquid ammonia, is formed by the action of acetamide in liquid ammonia solution, on metallic magnesium.

*Thallous Aquo-Ammono-Acetate*,  $\text{CH}_3\text{CONHTl}$  and  $\text{CH}_3\text{CONHTl} \cdot 2\text{NH}_3$ . The diammoniated salt is obtained by dissolving thallous nitride in acetamide solution and evaporating to crystallization. The diammoniated salt, when heated in vacuum, readily loses its ammonia of crystallization to form the anammonous salt.

*Potassium Aquo-Ammono-Propionate*,  $\text{C}_2\text{H}_5\text{CONHK}$ , has been obtained by the action of potassium amide on propionamide and also by warming propionitrile in liquid ammonia solution with potassium hydroxide.

*Sodium Aquo-Ammono-Propionate*,  $\text{C}_2\text{H}_5\text{CONHNa}$ .

*Potassium Aquo-Ammono-n-Butyrate*,  $\text{C}_3\text{H}_7\text{CONHK}$ .

*Potassium Aquo-Ammono-Isobutyrate*,  $\text{C}_3\text{H}_7\text{CONHK}$ .

*Potassium Aquo-Ammono-Isovalerate*,  $\text{C}_4\text{H}_9\text{CONHK}$ .

*Potassium Aquo-Ammono-n-Caproate*,  $\text{C}_5\text{H}_{11}\text{CONHK}$ .

All the above-listed salts are soluble in liquid ammonia and have been obtained well crystallized and of sharply definite composition.

*Potassium Aquo-Ammono-Palmitate*,  $\text{C}_{15}\text{H}_{31}\text{CONHK}$ , is formed as

\* Franklin and Stafford, *Am. Chem. J.*, **28**, 83 (1902); Franklin, *J. Am. Chem. Soc.*, **37**, 2279 (1915); Ruth V. Fulton, Thesis, Stanford University (1925); Cornell, *J. Am. Chem. Soc.*, **50**, 3311 (1928).

an insoluble, amorphous precipitate when potassium amide is added to a dilute solution of the slightly soluble palmitamide.

*Potassium Aquo-Ammono-Benzoate*,  $C_6H_5CONHK$ , is formed by the interaction of benzamide and potassium amide and also when benzonitrile in liquid ammonia solution is warmed with potassium hydroxide.<sup>5</sup>

*Sodium Aquo-Ammono-Benzoate*,  $C_6H_5CONHNa$ , has been prepared in a variety of ways which need not be detailed here. It has been observed to enter into many reactions which recall the behavior of sodium aquobenzoate.

Interesting examples of long-known metallic derivatives of acid amides are the following.

*Zinc Aquo-Ammono-Acetate*,  $(CH_3CONH)_2Zn$ .

*Mercuric Aquo-Ammono-Acetate*,  $(CH_3CONH)_2Hg$ .

*Zinc Aquo-Ammono-Butyrate*,  $(C_3H_7CONH)_2Zn$ .

*Zinc Aquo-Ammono-Benzoate*,  $(C_6H_5CONH)_2Zn$ .

*Mercuric Aquo-Ammono-Benzoate*,  $(C_6H_5CONH)_2Hg$ .

The zinc salts were prepared by the action of zinc ethyl on the respective acid amides.<sup>6</sup>

**Metallic Salts of Acidimides.** Two acetyl derivatives of water of the respective formulas,  $CH_3CO\cdot OH$  and  $CH_3CO\cdot O\cdot OCC_2H_5$ , are possible, the one being an acid the other an acid anhydride. On the other hand the trivalency of nitrogen permits the existence of three acetyl derivatives of ammonia, acetamide,  $CH_3CONH_2$ , diacetamide,  $(CH_3CO)_2NH$ , and triacetamide,  $(CH_3CO)_3N$ , the first and second of which are to be regarded as aquo-ammono acetic acids, the third as a mixed anhydride-anammonide of acetic acid. Examples of metallic salts of diacylamides are the following.<sup>7</sup>

*Potassium Aquo-Ammono-Diformate*,  $(HCO)_2NK$ .

*Sodium Aquo-Ammono-Diformate*,  $(HCO)_2NNa$ .

These salts of an aquo-ammono diformic acid have been prepared by the action of potassium and sodium respectively on formamide under petroleum ether.<sup>7</sup>

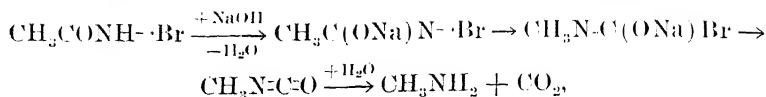
*Sodium Aquo-Ammono-Diacetate*,  $(CH_3CO)_2NNa$ , has been prepared by the action of metallic sodium on diacetamide using dry ether as solvent. When heated with methyl iodide methyl diacetamide, which is an N-methyl ester of an aquo-ammono diacetic acid, is formed,  $(CH_3CO)_2NNa + CH_3I = (CH_3CO)_2NCH_3 + NaI$ .

*Sodium Aquo-Ammono-Dibenzoate*,  $(C_6H_5CO)_2NNa$ . This salt has been prepared by the action of metallic sodium on dibenzamide

<sup>5</sup> Attempts made by Miss Fulton to prepare the dipotassium salt were unsuccessful. Dipotassium benzamide [Franklin and Stafford, *Am. Chem. J.*, 28 (1902)] should therefore be stricken from the list of known compounds.

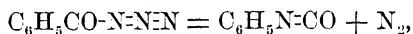
<sup>6</sup> Gal. *Bull. soc. chim.*, 2, 39, 647 (1883).

<sup>7</sup> Rakshit, *J. Chem. Soc.*, 103, 1557 (1913).

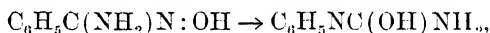


a further example of the intramolecular augmentation of acetic acid to a carbonic acid. The sodium salt of a mixed aquo-ammono acetic ammono hypobromous acid, formed by the action of sodium hydroxide on acetbromamide, undergoes rearrangement to form a compound which is at the same time an N-methyl ester, a sodium salt and a bromide of carbonic acid. Such a compound loses sodium bromide to form methyl isocyanate (N-methyl aquo-ammono-carbonate), which is readily hydrolyzed to methylamine and carbon dioxide.

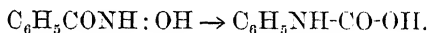
In a similar manner benzoylazine rearranges to form phenylisocyanate and nitrogen (nitrous anammonide),



benzamidoxime to form N-phenylurea,



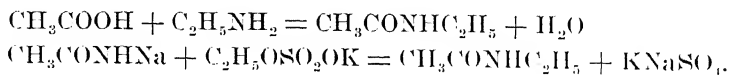
and benzhydroxamic acid to form N-phenylcarbamic acid,



N-phenylcarbamic acid breaks down partly into phenylisocyanate and water and partly into aniline and carbon dioxide.

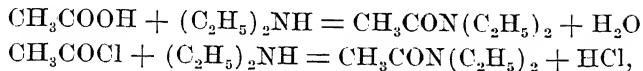
**Esters.** Representatives of each of the theoretically possible types of acid amide derivatives of the respective formulas,  $\text{RCONHR}$ ,  $\text{RC}(\text{NH})\text{OR}$ ,  $\text{RCONR}_2$  and  $\text{RC}(\text{NR})\text{OR}$ , are known, the methods of preparation and properties of which are such as to justify our regarding them as carboxylic acid esters.

*N-Esters*,  $\text{RCONHR}$ . Two equations which represent the formation of N-alkyl derivatives of acetamide are the following.



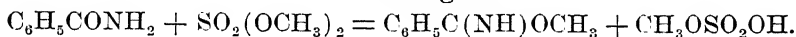
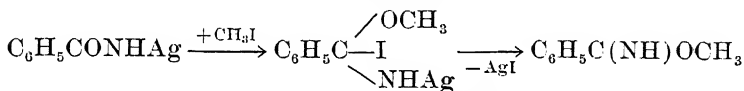
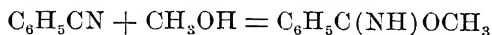
In accordance with the first equation N-ethyl aquo-ammono-acetate is formed by the action of an aquo acetic acid on an ammono ethyl alcohol. The second equation represents a reaction which is identical in principle with that involved in the formation of ethyl aquo-acetate by the action of potassium ethyl sulfate on sodium aquo-acetate.

*N-N-Esters*,  $\text{RCONR}_2$ . The equations,



represent the action respectively of aquo acetic acid and of acetyl chloride on an ammono ethyl alcohol to form *N-N*-diethyl aquo-ammono acetate.

*O-Esters*,  $\text{RC}(\text{NH})\text{OR}$ . Three methods for the formation of benzimidomethyl ester, which is an example of a carboxazyllic acid *O*-ester, are represented by the following equations,



The reaction represented by the first equation closely resembles that which takes place when methyl acetate and acetic acid are formed by the interaction of methyl alcohol and acetic anhydride. In the one case the ammono alcohol unites with an acid anammonide to form an acid ester, in the other the aquo alcohol reacts with an acid anhydride to form a mixture of the free acid and a neutral ester. The reactions represented by the second and third equations run parallel to those which take place when methyl benzoate is formed by the action respectively of methyl iodide on sodium aquobenzoate and of dimethyl sulfate on aquo benzoic acid.

*O-N-Esters*,  $\text{RC}(\text{NR})\text{OR}$ . *O-N*-Diethyl aquo-ammono-benzoate, as an example of this class of compounds, is formed by the action of sodium ethylate on *N*-ethylbenzimidochloride, which is an ester and at the same time a chloride of a benzoic acid, as represented by the equation,



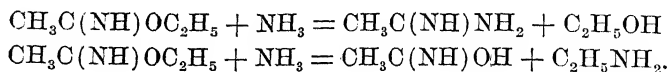
**Ammonolysis of Carboxazyllic Acid Esters.** But one acid amide *N*-ester has been investigated in respect to its ammonolytic behavior. Niemann<sup>15</sup> found that acetanilide is ammonolyzed to acetamide and aniline when heated in liquid ammonia solution with ammonium chloride,  $\text{CH}_3\text{CONHC}_6\text{H}_5 + \text{NH}_3 = \text{CH}_3\text{CONH}_2 + \text{C}_6\text{H}_5\text{NH}_2$ .

In liquid ammonia solution, as has been shown in this labora-

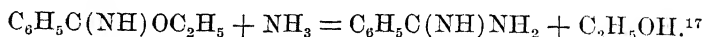
<sup>15</sup> Niemann, Thesis, Stanford University, 1926.



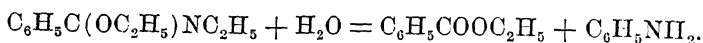
tory<sup>16</sup> acetimidoethyl ester used in the form of the hydrochloride undergoes ammonolytic decomposition as represented by the equations,



In alcoholic ammonia solution benzimidoethyl ester hydrochloride is ammonolyzed to benzamidine and ethyl alcohol,



The ammonolytic behavior of the O-N-esters has not been investigated. O-N-Diethyl aquo-ammono-benzoate is hydrolyzed under the action of aqueous hydrochloric acid to ethyl aquobenzoate and ethylamine,<sup>18</sup>



*Ester-Salts.* Regarding the two derivatives of acetamide represented by the formulas,  $\text{CH}_3\text{CONHC}_2\text{H}_5$  and  $\text{CH}_3\text{C}(\text{NH})\text{OC}_2\text{H}_5$ , as ethyl esters of aquo-ammono acetic acid it is clear that ethylacetamide and acetiminoethylester, and in general all compounds of the formulas,  $\text{RCONHR}$  and  $\text{RC}(\text{NH})\text{OR}$ , are formally acid esters and that as such they should be capable of forming metallic salts. Accordingly a considerable number of salts of acid esters of the first formula above are known, for example, sodium formanilide,  $\text{HCON}(\text{Na})\text{C}_6\text{H}_5$ , silver formanilide,  $\text{HCON}(\text{Ag})\text{C}_6\text{H}_5$ , sodium ethylacetamide,  $\text{CH}_3\text{CON}(\text{Na})\text{C}_2\text{H}_5$ , sodium acetanilide,  $\text{CH}_3\text{CON}(\text{Na})\text{C}_6\text{H}_5$ , and mercuric acetanilide,  $\text{CH}_3\text{CON}(\text{Hg})\text{C}_6\text{H}_5$ .

The acid N-esters of the carboxylic acids show their acid properties most strikingly perhaps by their action in liquid ammonia solution on metallic amides and nitrides. Only four salts as follows have been made by reactions carried out in this solvent. None the less the results obtained amply justify the conclusion that the method is capable of general application.<sup>19</sup>

*Silver N-Phenyl Aquo-Ammono-Acetate*,  $\text{CH}_3\text{CON}(\text{Ag})\text{C}_6\text{H}_5$  and  $\text{CH}_3\text{CON}(\text{Ag})\text{C}_6\text{H}_5\cdot\text{NH}_3$ . The ammonated salt separates well crystallized from a cold, concentrated solution of the salt formed by dissolving silver amide in a liquid ammonia solution of acet-

<sup>16</sup> Unpublished observations by H. S. King.

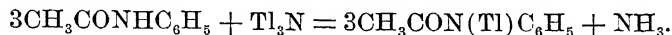
<sup>17</sup> Pinner, "Die Imidoäther," Berlin, 1892, p. 172.

<sup>18</sup> Lander, *J. Chem. Soc.*, 83, 320 (1903).

<sup>19</sup> Franklin, *J. Am. Chem. Soc.*, 37, 2292 (1915).

anilide. The ammonious salt is formed by heating the ammonated compound in vacuum to 100°.

*Thallous N-Phenyl Aquo-Ammono-Acetate*,  $\text{CH}_3\text{CON}(\text{Tl})\text{C}_6\text{H}_5$ . A solution of acetanilide converts black thallous nitride into the slightly soluble thallium salt. The action of the acid ester on the basic nitride is represented by the equation,

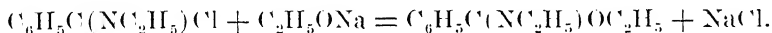


*Potassium N-Benzyl Aquo-Ammono-Acetate*,  $\text{CH}_3\text{CON}(\text{K})\text{CH}_2\text{C}_6\text{H}_5\cdot\text{NH}_3$ . The ammonated salt separates well crystallized from a highly concentrated, cold solution of the salt formed by the action of potassium amide on N-benzylacetamide.

*Potassium N-Phenetole Aquo-Ammono-Acetate*,  $\text{CH}_3\text{CON}(\text{K})\text{C}_6\text{H}_4\text{OC}_2\text{H}_5$ , is formed when phenetoleacetamide and potassium amide are brought together in liquid ammonia solution. The highly soluble salt separates from a cold, concentrated solution well crystallized.

Metallic salts of the iminoesters are not known nor have attempts been made to prepare them by reactions carried out in liquid ammonia solution been successful. As has already been noted acet-iminoethylester in liquid ammonia solution is ammonolyzed to acetamide and ethylamine in the presence of potassium amide (p. 280).

*O-N-Esters*,  $\text{RC}(\text{NR})\text{OR}$ . O-N-Diethyl aquo-ammono-benzoate, as an example of this class of compounds, is formed by the action of sodium ethylate on ethyl benzimide-chloride, which is an ester and at the same time a chloride of a benzoic acid, as represented by the equation,



The ammonolytic behavior of this compound has not been investigated. It is hydrolyzed under the action of aqueous hydrochloric acid to ethyl benzoate and ethylamine.<sup>20</sup>

<sup>20</sup> Lander, *J. Chem. Soc.*, 83, 320 (1903).

## CHAPTER XXX.

### HYDROCYANIC ACID AND THE NITRILES.

An aquo aldehyde is characterized by the presence of a carbonyl group in combination with two hydrogen atoms or with one hydrogen atom and an alkyl or aryl group as represented by the familiar formulas,  $\text{H}_2\text{C}=\text{O}$  and  $\text{RCH}=\text{O}$ . When both valences of the carbonyl group are occupied by hydrocarbon radicals as represented by the formula,  $\text{R}_2\text{C}=\text{O}$ , the compounds so constituted are aquo ketones. Since now the groups,  $=\text{C}=\text{N}-$  and  $-\text{C}\equiv\text{N}$ , contained respectively in the Schiff bases,  $\text{CH}_2=\text{NR}$ ,  $\text{RCH}=\text{NR}$ , and  $\text{R}_2\text{C}=\text{NR}$  and in the nitriles,  $\text{HC}\equiv\text{N}$  and  $\text{RC}\equiv\text{N}$ , are the nitrogen analogs of the carbonyl group, or as nearly so as the trivalency of nitrogen permits, it follows that not only the Schiff bases but also the nitriles should show many of the properties of the aldehydes and ketones.

We have already discussed in some detail the Schiff bases as aldehyde-ethers and ketone-ethers of the nitrogen system. In the following it will be shown that hydrocyanic acid shows certain characteristically aldehydic properties and that the nitriles simulate in a variety of ways the behavior of the ketones.

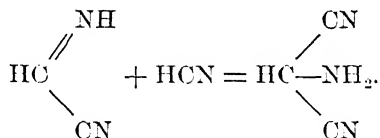
It is to be observed in this connection that the carbylic acids, that is to say the carboxylic acids, the acid amides and the acid amidines, are by no means devoid of aldehydic properties. For example, acetic acid reacts with hydroxylamine to form acethydroxamic acid,  $\text{CH}_3\text{C}(\text{OH})\text{N}:\text{OH}$ , and with phenylhydrazine to form acetylphenylhydrazide,  $\text{CH}_3\text{C}(\text{OH})\text{N}:\text{NH}\text{C}_6\text{H}_5$ . Acetyl hydrazide,  $\text{CH}_3\text{C}(\text{OH})\text{N}:\text{NH}_2$ , is formed by the action of hydrazine on acetamide, and certain aromatic amidines have been found to react with hydroxylamine to form amidoximes,  $\text{RC}(\text{NH}_2)\text{N}:\text{OH}$ . Acetic acid in the form of its ethyl ester undergoes the aldol condensation when it is converted into acetoacetic ester. These reactions show that the carbonyl group and the carbimide group contained in the carbylic acids carry into these compounds some of the properties characteristic of the aldehydes and ketones.

**Hydrocyanic Acid.** It has been shown in Chapter XII that hydrocyanic acid, when represented by the formula,  $\text{HC}\equiv\text{N}$ , is to be looked upon as an ammonio carbonous acid, and that the metallic salts of hydrocyanic acid and the alkyl and aryl isocyanides are metallic carbonites and carbonous acid esters respectively of the

nitrogen system. Furthermore, in another place (*cf.* Chapter XXVI) the relationships existing between formamide and formamidine, on the one hand, and hydrocyanic acid, on the other, have been interpreted on the assumption that hydrocyanic acid represented by the formula HCN is formic anammonide. It is here proposed to show that hydrocyanic acid exhibits distinctly many of the properties of the simpler aliphatic aldehydes. It undergoes polymerization and condensation as formaldehyde does. It forms acid sulfite, water and alcohol addition products, reacts with hydroxylamine and hydrazine, and may be reduced to an ammono alcohol and oxidized to an ammono carbonic acid, as is shown in some detail below.

*Polymerization.* In the presence of alkalis or salts hydrocyanic acid undergoes polymerization to brown amorphous substances of unknown constitution.

*Aldol Condensation.* Hydrocyanic acid undergoes condensation in a manner closely analogous to the familiar aldol condensation of the aldehydes. Just as formaldehyde condenses to glycolaldehyde,  $2\text{CH}_2\text{O} = \text{CH}_2(\text{OH})\text{CHO}$ ,<sup>1</sup> so hydrocyanic acid similarly condenses, and contingent upon the presence of the triple bond in the cyanogen group, first as represented by the equation,  $2\text{HCN} = \text{HC}(\text{NH})\text{CN}$ , to an uncertainly known<sup>2</sup> iminoacetonitrile and thence to aminomalalonitrile<sup>3</sup> in accordance with the equation,



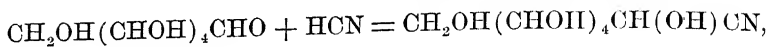
The reactions represented by these equations resemble the benzoin condensation rather more closely than they do aldol formation.

*The Cyanhydrine Reaction.* Just as the transformation of formaldehyde into glycolaldehyde consists in an aldol condensation taking place between two molecules of aquo formaldehyde and as the analogous formation of aminomalalonitrile involves a similar condensation of hydrocyanic acid so the cyanhydrine reaction represented by the equation,  $\text{CH}_2\text{O} + \text{HCN} = \text{CH}_2(\text{OH})\text{CN}$ , is to be regarded as an aldol condensation taking place between aquo formaldehyde and hydrocyanic acid. The familiar formation of a cyanhydrine by the action of hydrocyanic acid on glucose,

<sup>1</sup> Euler and Euler, *Ber.*, **39**, 51 (1906).

<sup>2</sup> Nef, *Ann. Chem.*, **287**, 337 (1895); Willstätter and Wirth, *Ber.*, **42**, 1915 (1909); Michael and Hibbert, *Ann. Chem.*, **364**, 70 (1909), give this compound the formula  $\text{HN}:\text{CH}:\text{NC}$ .

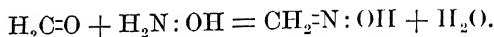
<sup>3</sup> Lange, *Ber.*, **6**, 99 (1873); Wippermann, *Ber.*, **7**, 768 (1874).



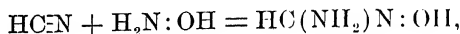
may be said to involve an aldol condensation.

*The Acid Sulfitc Addition Product.* Another characteristic property of the aldehydes is that of reacting with sodium or potassium acid sulfitc to form the well-known addition products. In an entirely similar manner hydrocyanic acid reacts with potassium acid sulfitc<sup>4</sup> to form a compound of the formula,  $\text{HC}(\text{NH}_2)(\text{SO}_2\text{OK})_2$ , which is obviously an approximate analog of the compound,  $\text{CH}_2(\text{OH})\text{SO}_2\text{OK}$ , obtained by the action of acid potassium sulfitc on formaldehyde.

*Action of Hydroxylamine.* Formaldehyde reacts with hydroxylamine yielding formaldoxime,



In a very similar manner hydrocyanic acid is acted upon by hydroxylamine as represented by the equation,

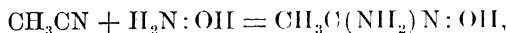


to form formamidoxime.<sup>6</sup> In the one reaction water is completely separated, in the other the analogous elimination of ammonia extends only to the formation of the amido group. For complete separation of ammonia the reaction between hydrocyanic acid and hydroxylamine would have to take the course represented by the equation,  $2\text{HC}\equiv\text{N} + 3\text{H}_2\text{N}:\text{OH} = (\text{HC})_2(\text{N}:\text{OH})_3$ , to give an oxime which is not known.

**The Nitriles,  $\text{RCN}$ .** It has already been shown that the nitriles are to be regarded as acid anammonides (*cf.* Chapter XXVI). Here it will be pointed out that in some respects they behave in a manner closely resembling that of the ketones.

*Polymerization.* Excepting phenyl cyanide, which has been converted into a trimer known as cyaphenine, none of the nitriles has been obtained in its trimolecular form. In this absence of any marked tendency to undergo trimerization the nitriles resemble the ketones. Ordinary acetone, it will be recalled, does not form a trimer.

*Action of Hydroxylamine.* Methyl cyanide reacts with hydroxylamine in accordance with the equation,

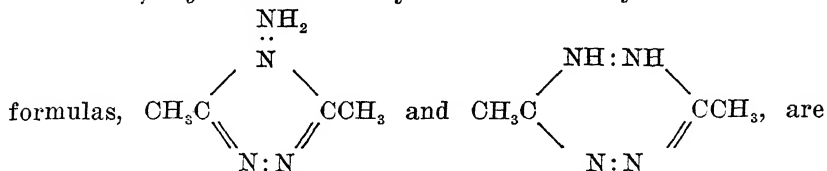


<sup>4</sup> v. Pechmann and Manck, *Ber.*, **28**, 2374 (1895).

<sup>6</sup> Lossen and Schifferdecker, *Ann. Chem.*, **166**, 294 (1873).

to form acetamidoxime. The reaction involved is clearly similar to that which takes place when the same reagent acts on acetone to yield acetoxime,  $(\text{CH}_3)_2\text{C}:\text{N}:\text{OH}$ . In the latter reaction the carbonyl oxygen is eliminated as water, whereas in the former the elimination of nitrile nitrogen goes only to the extent of forming an amide group.

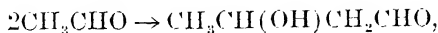
*Action of Hydrazine.* Two cyclic acetic acid hydrazides of the



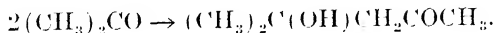
known respectively as 4-amino-3-5-dimethyl-1-2-4-triazole and 3-6-dimethyl-1-2-dihydro-1-2-4-5-tetrazine, have been obtained by the action of hydrazine on acetonitrile.<sup>7</sup>

It may be assumed that an acetic acid hydrazide of the formula,  $\text{CH}_3\text{C}(\text{NH})\text{NH}:\text{NH}_2$ , is first formed, following which two molecules of this hydrazide interact with the loss of ammonia to form the cyclic hydrazides. It is known that the acetic acid hydrazide,  $\text{CH}_3\text{CONH}:\text{NH}_2$ , when heated at  $180^\circ$  loses water and passes over into 4-amino-3-5-dimethyl-1-2-4-triazole.<sup>8</sup>

*Aldol Condensation.* The aliphatic nitriles like the ketones tend to undergo condensation reactions rather than to form polymerization products. Methyl cyanide, for example, under the influence of metallic sodium, or better of sodium amide, undergoes condensation to form  $\beta$ -iminobutyronitrile as represented by the equation,  $2\text{CH}_3\text{CN} \rightarrow \text{CH}_3\text{C}(\text{NH})\text{CH}_2\text{CN}$ .<sup>9</sup> The reaction involved in the formation of this compound, which is at the same time an ammono ketone-alcohol and a butyric anammonide, resembles closely the condensation of acetaldehyde to  $\beta$ -hydroxy butyric aldehyde,



and of acetone to diacetone alcohol,



All three of these reactions involve typical aldol condensations.

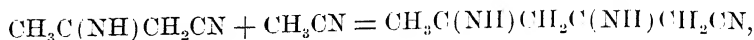
*Formation of Cyanmethine.* When the product obtained by treating acetonitrile in ether solution with metallic sodium, presumably an

<sup>7</sup> Curtius, Darapsky and Müller, *Ber.*, **48**, 1632 (1915).

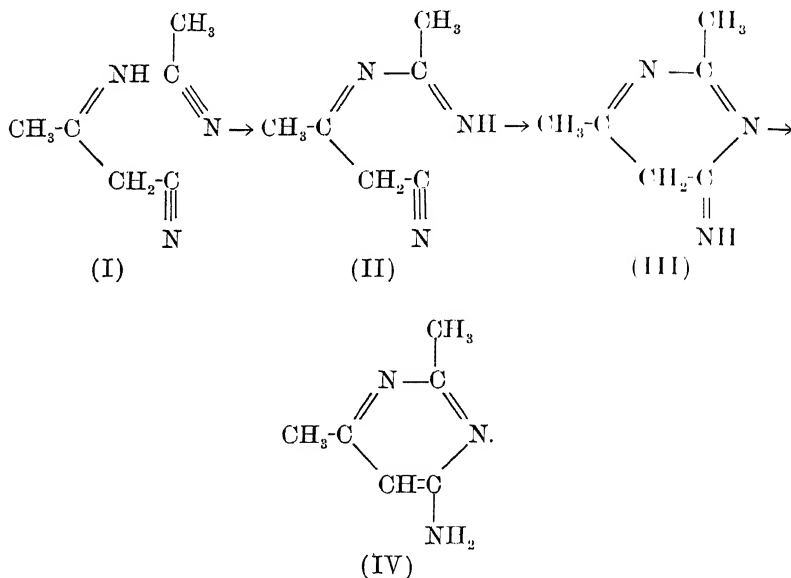
<sup>8</sup> Pellizzari, *Gazz. chim. ital.*, **39**, I, 535.

<sup>9</sup> E. von Meyer, *J. prakt. Chem.*, [2] **27**, 152 (1883), **38**, 336 (1888), **78**, 497 (1908); Holzwardt, *J. prakt. Chem.*, [2] **39**, 244 (1889).

impure salt of  $\beta$ -iminobutyronitrile, is heated with acetonitrile in a closed tube for a time at  $140^\circ$ , cyanmethine is formed.<sup>10</sup> Acetonitrile entering into reaction with  $\beta$ -iminobutyronitrile, formed as explained above, instead of forming an ammono aldol of the formula,  $\text{CH}_3\text{C}(\text{NH}_2)(\text{CH}_2\text{CN})_2$ , as might be expected in view of the behavior of hydrocyanic acid, or of undergoing an aldol condensation with  $\beta$ -iminobutyronitrile in accordance with the equation,



as a matter of fact reacts with the aldol,  $\text{CH}_3\text{C}(\text{NH})\text{CH}_2\text{CN}$ , after a manner which, in principle, is identical with that followed by formaldehyde, acetaldehyde and benzonitrile in polymerizing to their respective trimolecular modifications and with that followed by the ammono formaldehyde-acetal,  $\text{CH}_2=\text{N}-\text{CH}_2-\text{N}-\text{CH}_2$ , in dimerizing to hexamethylenetetramine. The action of methyl cyanide on  $\beta$ -iminobutyronitrile may be represented by the scheme,



Acetic anammonide unites successively with the ammono ketone imino group and the acid anammonide ends of the  $\beta$ -iminobutyronitrile molecule (I) to form the cyclic compound (III). The reaction concerned in passing from (I) to (II) involves a ketone-acetal formation, that in the transformation of (II) to (III) the

<sup>10</sup> Holtzworth, *J. prakt. Chem.*, [2] 39, 244 (1889).

ammonation of a carbylic acid anammonide group. The compound (III), by intramolecular rearrangement in principle a keto-enol transformation, passes over into (IV) which represents a pyrimidine derivative long known as cyanmethine. It is to be observed that formulas (III) and (IV) contain residues of ammono acetic acid,  $\text{CH}_3\text{C}(\text{NH})\text{NH}_2$ , and of the nitrogen analog of acetoacetic acid,  $\text{CH}_3\text{C}(\text{NH})\text{CH}_2\text{C}(\text{NH})\text{NH}_2$ .



## CHAPTER XXXI.

### NITROSAMINES AND DIAZO COMPOUNDS.

Speculating upon the possible existence of a nitrous acid of the nitrogen system and of a nitrous acid derived at the same time from ammonia and water we are led to write the formula,  $\text{H}_2\text{N} \cdot \text{N} \cdot \text{NH}$ , for an ammono nitrous acid and  $\text{H}_2\text{N} \cdot \text{N} \cdot \text{O}$  or  $\text{HN} \cdot \text{N} \cdot \text{OH}$ , for an aquo-ammono nitrous acid.<sup>1</sup>

Neither of these compounds is known. Reactions which might be expected to give the first compound yield instead nitrogen and ammonia, the second, if formed, decomposes immediately to nitrogen and water.

While such compounds have not been prepared<sup>2</sup> either in the free state or in the form of salts, it is none the less true that many compounds are known which are to be regarded as derivatives of these hypothetical acids. For example, phenyltriazene,  $\text{C}_6\text{H}_5\text{N} \cdot \text{N} \cdot \text{NH}_2$ , and diazoaminobenzene,  $\text{C}_6\text{H}_5\text{N} \cdot \text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$ , are esters of an ammono nitrous acid, dimethylnitrosamine,  $(\text{CH}_3)_2\text{N} \cdot \text{N} \cdot \text{O}$ , and diazobenzene,  $\text{C}_6\text{H}_5\text{N} \cdot \text{N} \cdot \text{OH}$ , are esters of an aquo-ammono nitrous acid. Metallic salts of phenyltriazene, diazobenzene and diazoaminobenzene are known.

#### NITROSAMINES

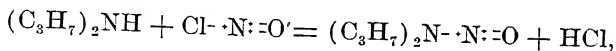
Assuming, as has been done above, that dimethylnitrosamine is an ester of an aquo-ammono nitrous acid it follows that its formation by the action of nitrous acid on dimethylamine in accordance with the equation,  $(\text{CH}_3)_2\text{NH} + \text{HONO} = (\text{CH}_3)_2\text{N} \cdot \text{N} \cdot \text{O} + \text{H}_2\text{O}$ ,

<sup>1</sup> For an explanation of the sense in which the small plus and minus signs are here used the reader is referred to Chapter IV. Although it is perhaps questionable whether one has a right to say that the middle nitrogen atom is positive in respect to the two end nitrogen atoms as represented by the first formula and that the second nitrogen atom is positive as indicated in the second and third, it will nevertheless appear as we proceed that the use of these formulas in discussing the nitrosamines and the diazo compounds is in a proper enough sense justifiable.

<sup>2</sup> Dimroth and Pfister [*Ber.*, 43, 2767 (1910)] report the fugitive existence of triazene (ammono nitrous acid) in water solution at low temperatures. Fernelius and Watt [*J. Am. Chem. Soc.*, 55, 3482 (1933)] were unable to prepare metallic salts of aquo-ammono nitrous acid by the action of metallic amides on certain diarylnitrosamines. Nitrosamide is known in liquid ammonia solution. [Schwarz and Giese, *Ber.*, 67, 1108 (1934).] It is interesting in this connection to recall that aquo nitrous acid is unknown in the free state excepting in so far as it may be assumed to exist in aqueous solution.

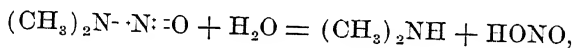
is to be explained as consisting in the esterification of an ammono methyl alcohol to an N-N-dimethyl aquo-ammono-nitrite.

Di-n-propylnitrosamine has been prepared by the action of nitrosylchloride on di-n-propylamine,

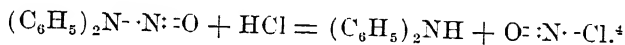


which is to say that an ester of an aquo-ammono nitrous acid is formed by the action of a nitrous acid chloride<sup>3</sup> on an ammono propyl alcohol. The reaction, in principle, is identical with that which takes place when ethyl acetate is formed by the action of acetyl chloride on ordinary ethyl alcohol. The formation of alkyl nitrites by the action of nitrosyl chloride on aquo alcohols has apparently never been observed.

The nitrosamines are readily decomposed by the action of aqueous hydrochloric acid, though not by potassium hydroxide, into secondary amines and aquo nitrous acid. Dimethylnitrosamine, for example, undergoes hydrolytic decomposition,

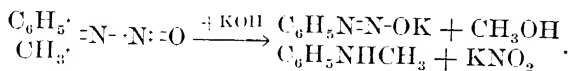


to form an ammono methyl alcohol and aquo nitrous acid. By the action of hydrochloric acid gas on diphenylnitrosamine diphenylamine and nitrosylchloride are formed,



An N-N-diphenyl aquo-ammono-nitrite is converted into an ammono phenol and a nitrous acid oxide-chloride.

Under the action of fused potassium hydroxide phenylmethylnitrosamine yields, among other products, potassium isodiazobenzene methylaniline and potassium nitrite.<sup>5</sup> It is reasonable to explain the formation of these compounds as resulting from the hydrolysis of phenylmethylnitrosamine in accordance with the equation,



A part of the N-phenyl-N-methyl aquo-ammono-nitrite is hydrolyzed to a phenyl potassium aquo-ammono-nitrite and aquo methyl alco-

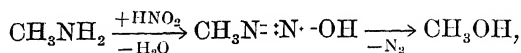
<sup>3</sup> It is interesting to note that nitrosylchloride acts as a nitrous acid chloride whereas the chloramines act in general as ammono hypochlorous acids (*cf.* Chapter XXI), nitrogen chloride as a hypochlorous anammonide. (Chapter XIX.)

<sup>4</sup> Lachman, *Ber.*, 33, 1038 (1900).

<sup>5</sup> Bamberger, *Ber.*, 27, 1179 (1894).

hol, another part to an ammono alcohol (methylaniline) and potassium aquo-nitrite.

As is well known the action of aquo nitrous acid on primary amines results in their conversion into aquo alcohols. For example, when nitrous acid acts on methylamine it may be assumed, ignoring the primary formation of methylammonium nitrite, that in accordance with the equation,



an N-methyl aquo-ammono-nitrite is formed which decomposes to yield aquo methyl alcohol and nitrogen. It may be reasonably assumed that the nitrogen initially separates as nitrous anammonide,  $\text{N}::\text{N}$ . Examples of mixed acids containing residues of ammono nitrous acid and aquo-ammono nitrous acid are listed elsewhere (*cf.* Chapter XX).

#### DIAZO COMPOUNDS

In a review of Cain's "Chemistry and Technology of the Diazo-Compounds,"<sup>6</sup> Stieglitz<sup>7</sup> wrote in part as follows.

"In the treatment of the subject, a point of view is missed which, it is thought would make possible a clearer, simpler and more systematic presentation of diazo compounds—that is a *more pronounced and systematic* presentation of them simply as derivatives of the nitrous acid radical N. In many of their most characteristic reactions (with phenols, anilines, diketones, nitroparaffins, sulfites, in their molecular rearrangements, tautomerisms, etc.), diazo compounds duplicate the behavior of the mother substance, nitrous acid, its salts, esters and other derivatives, and to a certain extent we have also the recurrence of the same problems which have been worked out for the aniline derivatives of other acids. In many ways it seems unfortunate that the word "diazo" was ever coined or that it cannot well be eliminated now. The functions of the two nitrogen atoms forming the "diazo group" are of course so radically different and so persistently recognizable throughout all transformations that they might almost be atoms of two different elements. . . . We have here exactly the same difference as between the radical Cl of hypochlorous acid and that of hydrochloric acid whose functions are fundamentally different, . . ."

It is apparent from this quotation that Stieglitz clearly recognizes the diazo compounds as derivatives of nitrous acid, that is to say of tripositive or nitrous acid nitrogen, a view which to the best of the writer's knowledge is nowhere else so clearly recorded in the literature of the diazo compounds.<sup>9</sup>

<sup>6</sup> Edward Arnold, London, 1908.

<sup>7</sup> Stieglitz, *J. Am. Chem. Soc.*, **30**, 1797 (1908).

<sup>9</sup> Wieland, "Die Praxis des organischen Chemikers" (Gattermann), 21st Ed., Berlin and Leipzig, 1928.

It will be our endeavor in this chapter to show that the diazo compounds are derivatives of nitrous acid.

Diazobenzene. According to Hantzsch<sup>10</sup> diazobenzene exists in four isomeric forms, (1) as benzenediazonium hydroxide,  $\text{C}_6\text{H}_5\text{N}-\text{OH}$ ,  
 $\begin{array}{c} ||| \\ \text{N} \end{array}$ ,  
 (2) and (3) as syn<sup>11</sup> and anti-diazobenzene hydroxide,  $\text{C}_6\text{H}_5\text{N}$   
 $\begin{array}{c} || \\ \text{HO}-\text{N} \end{array}$  and  
 $\text{C}_6\text{H}_5\text{N}$   
 $\begin{array}{c} || \\ \text{N}-\text{OH} \end{array}$ , and (4) as phenylnitrosamine or pseudo anti-diazobenzene hydroxide,  $\text{C}_6\text{H}_5\text{NH}-\text{NO}$ .<sup>12</sup>

Angeli<sup>13</sup> accepts formula (1) for benzenediazonium hydroxide but in opposition to Hantzsch maintains that normal (labile, syn-) diazobenzene has the constitution represented by the formula,  $\text{C}_6\text{H}_5\text{N}(\text{NH})\text{O}$ ,<sup>14</sup> while to the iso (stable, anti,) diazobenzene he ascribes either of the formulas,  $\text{C}_6\text{H}_5\text{N}=\text{N}-\text{OH}$  or  $\text{C}_6\text{H}_5\text{NH}-\text{N}=\text{O}$ . In this chapter we shall for the most part use these two formulas more or less indifferently to represent the several forms of diazobenzene. From time to time it will be helpful to use the formulas,  $\text{C}_6\text{H}_5\text{N}::\text{N}-\text{OH}$  and  $\text{C}_6\text{H}_5\text{NH}-\text{N}::\text{O}$ , in which the one nitrogen atom is represented as ammonia nitrogen and the other as nitrous acid nitrogen respectively.

**Formation.** 1. Benzenediazonium salts are formed by the action of nitrous acid on aniline in acid solution. When benzenediazonium chloride is treated with potassium hydroxide solution the potassium salt of normal diazobenzene is formed. When this salt is heated with concentrated potassium hydroxide solution at 130° it is converted into the potassium salt of isodiazobenzene. Whether these compounds are stereoisomers, as claimed by Hantzsch, or possibly structural isomers, as maintained by Angeli, we must leave here an open question.

2. Normal diazobenzene is formed in fair yield by the action of hydroxylamine on nitrosobenzene in alkaline alcoholic solution.<sup>15</sup>

Interpreting the reactions involved on the assumption that no augmentation and reduction reactions intervene, in other words that the nitrosobenzene and hydroxylamine residues maintain their

<sup>10</sup> Hantzsch and Reddell, "Die Diazoverbindungen," Berlin, 1921.

<sup>11</sup> The syn- form is known in the form of metallic salts.

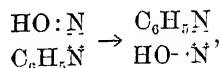
<sup>12</sup> This compound has not been isolated. 4-Nitrophenylnitrosamine is known.

<sup>13</sup> References to the papers of Angeli and of Hantzsch are too numerous to be cited here. See Beilstein, "Handb. org. Chem.," 4th Ed., 16, 426 (1933).

<sup>14</sup> This formula may be said to represent nitrobenzene in which one of the oxygen atoms is replaced by the imide group.

<sup>15</sup> Hantzsch, *Ber.*, 38, 2056 (1905). According to Bamberger [*Ber.*, 28, 1218 (1895)], isodiazobenzene is formed.

identities in the reaction product, it would be reasonable to conclude that hydroxylamine acts on nitrosobenzene as represented by the equation,  $\text{C}_6\text{H}_5\text{N}::\text{O} + \text{H}_2\text{N}::\text{OH} = \text{C}_6\text{H}_5\text{N}::\text{N}::\text{OH} + \text{H}_2\text{O}$ ,<sup>16</sup> to form an oxime of nitrosobenzene. If normal diazobenzene is in fact an ester of aquo-ammonio nitrous acid, and not an oxime of nitrosobenzene, it would seem to follow that the above-assumed primary product of the interaction of hydroxylamine and nitrosobenzene undergoes a Beckmann-like rearrangement,

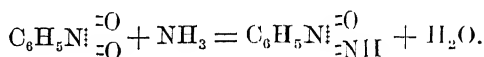


in that an exchange of positions on the part of the phenyl and hydroxyl groups involves the intramolecular augmentation of the phenyl to nitroso nitrogen bond and the reduction of hydroxylamine to ammonia nitrogen and water oxygen.

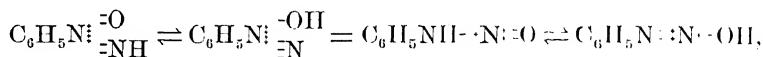
3. The sodium salts of normal diazobenzene and isodiazobenzene are formed, in very small amounts it is to be noted, by the action of sodium amide, suspended in petroleum ether, on nitrobenzene.

A fair yield of diazobenzene, identified in the form of phenyl azo- $\beta$ -naphthol, has been obtained by the action of potassium amide on nitrobenzene in liquid ammonia solution.<sup>18</sup>

Deducing the structure of normal diazobenzene from these methods of preparation one is led to conclude that normal diazobenzene is derived from nitrobenzene by the substitution of an NH group in place of one of the oxygen atoms in nitrobenzene,



The rearrangement of this formula for diazobenzene into the generally accepted formula,



involves the intramolecular augmentation of the phenyl to nitroso nitrogen bond and the concomitant reduction of nitrogen as it exists in nitrobenzene to nitrous acid nitrogen.<sup>18a</sup>

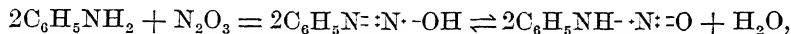
<sup>16</sup> The reader will recall that the colon is used to represent bonds concerning the polarity of which no opinion is expressed.

<sup>17</sup> Bamberger and Wetter, *Ber.*, 37, 629 (1904).

<sup>18</sup> Bergstrom and Fernelius, *Chem. Revs.*, 12, 151 (1933).

<sup>18a</sup> If Angeli is right in his view of the structure of normal diazobenzene hydroxide, it appears that benzenediazonium hydroxide is to be looked upon as a tautomer of normal diazobenzene hydroxide represented by the second of the preceding tautomeric formulas.

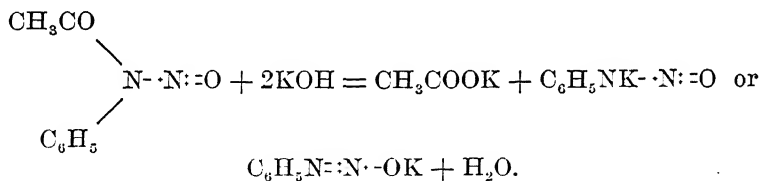
4. By the action of nitrous anhydride (a solution of  $\text{NO}_2$  and  $\text{NO}$  in chloroform) on aniline in ether solution Bamberger<sup>19</sup> obtained isodiazobenzene which he isolated in the form of its sodium salt. On the assumption that the reaction involved takes place as represented by the equation,



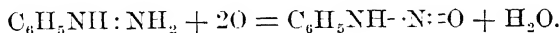
it is fair to conclude that isodiazobenzene is an N-phenyl ester of an aquo-ammono nitrous acid formed by the action of nitrous anhydride on aniline which is an ammono phenol.

5. The potassium salt of normal diazobenzene is formed by the action of a strong aqueous solution of potassium hydroxide on nitroacetanilide.<sup>20</sup>

It may be said that by the hydrolytic action of potassium hydroxide a phenyl ester of a mixed aquo-ammono acetic aquo-ammono nitrous acid is converted into potassium aquoacetate and the potassium salt of N-phenyl aquo-ammono nitrous acid as represented by the equation,



6. Under the action of mercuric oxide phenylhydrazine, in the form of its sulfate, is oxidized to diazobenzene sulfate or is converted into equimolecular quantities of phenylazide and aniline depending upon whether mercuric oxide or phenylhydrazine is kept in excess.<sup>21</sup> Under the first conditions phenylhydrazine is oxidized to a phenyl aquo-ammono-nitrite as follows,



The formation of phenylazide and aniline by the interaction of phenylhydrazine and diazobenzene will be discussed in the following chapter.

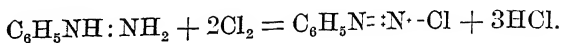
7. Diazobenzene chloride is formed by the action of chlorine on

<sup>19</sup> Bamberger, *Ber.*, 27, 1948 (1894).

<sup>20</sup> Hantzsch and Wachter, *Ann. Chem.*, 325, 229 (1920); Bamberger, *Ber.*, 27, 915 (1894), 30, 266 (1897).

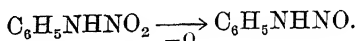
<sup>21</sup> E. Fischer, *Ann. Chem.*, 190, 98 (1878).

phenylhydrazine in glacial acetic acid solution.<sup>22</sup> A derivative hydrazine is augmented to a phenylnitrous acid chloride,

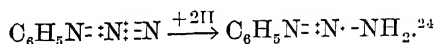


At the same time elementary chlorine is reduced to hydrochloric acid chloride.

S. Diazobenzene has been obtained by the action of reducing agents on phenylnitramide.<sup>23</sup> The reactions involved consist in the reduction of a phenyl aquo-ammonio-nitrate to a phenyl aquo-ammonio-nitrite as represented by the equation,

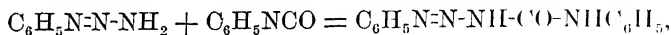


Diazobenzeneamide, Phenyltriazene,  $\text{C}_6\text{H}_5\text{N}::\text{N}\cdot\text{NH}_2$ . The formation of phenyltriazene by the action of a cold solution of stannous chloride and hydrochloric acid on phenylazide,

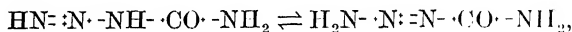


may be regarded as consisting in the reduction of a phenyl ammonio-nitrate to a phenyl ammonio-nitrite.

Diazobenzeneamide reacts with phenylisocyanide,



to form benzeneazophenylurea.<sup>25</sup> This compound is to be looked upon as a diphenyl ester of an ammonio nitrous aquo-ammonio carbonic acid,



and not as an azo compound. Of this distinctly acid compound Dimroth prepared the potassium, sodium and silver,  $\text{C}_{13}\text{H}_{11}\text{ON}_4\text{Ag}$  salts, the first two of which were not analyzed.

**Augmentation of Diazo Compounds.** Regarding diazobenzene hydroxide and diazobenzeneamide as derivatives respectively of an aquo-ammonio nitrous acid and an ammonio nitrous acid one would expect them to be susceptible to the action of augmenting agents

<sup>22</sup> Chattaway, *J. Chem. Soc.*, 93, 852 (1908).

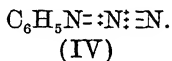
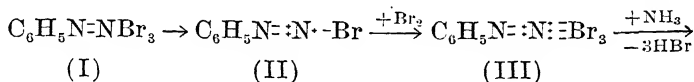
<sup>23</sup> Bamberger and Landsteiner, *Ber.*, 26, 492 (1893); Bamberger, *Ber.*, 27, 1181 (1894).

<sup>24</sup> Dimroth, *Ber.*, 2376 (1907).

<sup>25</sup> Dimroth, *Ber.*, 40, 2387 (1907).

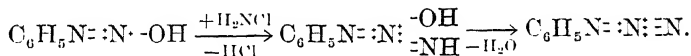
As a matter of fact many reactions are known which involve the augmentation of diazo compounds.

1. The interaction of diazobenzene perbromide and ammonia to form phenylazide, as first accomplished by Griess<sup>26</sup> may be explained as consisting in the conversion of a phenyl nitrous acid bromide into a phenyl ammononitrate by the augmenting action of bromine. As well as by any one of several others which might be written the reactions involved are represented by the scheme,



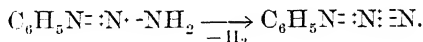
The perbromide (I), for present purposes, may be regarded as diazobenzene bromide (II) and free bromine. The bromine augments the nitrous acid ester-bromide (II) to the nitric acid ester-bromide (III) which, under the action of ammonia, is ammonolyzed to the phenyl ammononitrate (IV) and hydrobromic acid.

2. In a paper entitled "Azotization by Chloramine," Forster,<sup>27</sup> describes the formation of phenylazide by the action of monochloramine on diazobenzene in cold, neutral aqueous solution. One of the several mechanisms whereby the reactions involved may be explained is represented by the scheme,



It is assumed that the ammono hypochlorous acid augments the phenyl aquo-ammono-nitrite to a phenyl aquo-ammono-nitrate and that this unknown compound loses water to yield phenylazide.

So also is phenylazide formed by the augmenting action of sodium hypobromite and of silver nitrate on diazobenzeneamide.<sup>28</sup>



3. By the action of augmenting agents, such as sodium hypobromite, potassium ferricyanide and potassium permanganate, diazobenzene has been converted into phenylnitramide.<sup>29</sup> The reactions involved, which may be represented by the equation,

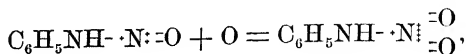
<sup>26</sup> Griess, *Ann. Chem.*, **137**, 68 (1866).

<sup>27</sup> Forster, *J. Chem. Soc.*, **107**, 263 (1915).

<sup>28</sup> Dimroth, *Ber.*, **40**, 2388 (1897).

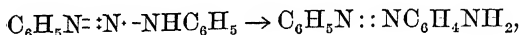
<sup>29</sup> Bamberger and Storch, *Ber.*, **26**, 477 (1893); Bamberger and Landsteiner, *Ber.*, 485 (1893).





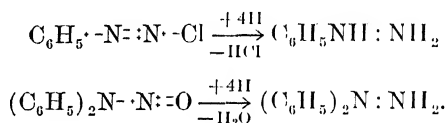
consist in the oxidation of an N-phenyl aquo-ammono-nitrite to an N-phenyl aquo-ammono-nitrate and are identical in principle with those discussed under paragraphs 1 and 2 above in that in each case nitrous acid nitrogen is augmented to nitric acid nitrogen.

4. The rearrangement of diazoaminobenzene to aminoazobenzene,

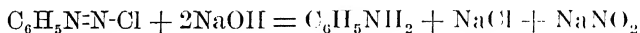


may be said to consist of the intramolecular reduction of a diazo compound to an azo compound and the concomitant augmentation of a phenyl group to a phenylene group.

**Reduction of Diazo Compounds.** By the action of reducing agents certain aryl derivatives of aquo-ammono nitrous acid are converted into the corresponding derivatives of hydrazine. For example, diazobenzene chloride in hydrochloric acid solution is reduced to phenylhydrazine by the action of stannous chloride,<sup>30</sup> and diphenylnitrosamine, in dilute acetic acid solution, is reduced to unsymmetrical diphenylhydrazine by the action of zinc dust.<sup>31</sup> The respective reactions, which, in principle, involve the reduction of nitrous acid to hydrazine, are represented by the equations,



**Hydrolysis of Diazobenzene.** 1. Boiling concentrated sodium hydroxide solution acts on diazobenzene chloride to give good yields of sodium aquonitrite.<sup>32</sup> The reaction involved may be represented by the equation,



and said to consist in the hydrolysis of an aquo-ammono nitrous acid ester to form aniline and sodium aquonitrite. However aniline was not identified among the reaction products.

2. Bamberger<sup>33</sup> found that aquo nitrous acid is set free when

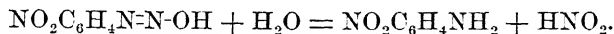
<sup>30</sup> Meyer and Lecco, *Ber.*, **16**, 2976 (1883).

<sup>31</sup> E. Fischer, *Ann. Chem.*, **190**, 146 (1878).

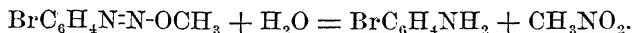
<sup>32</sup> v. Pechmann and Frobenius, *Ber.*, **27**, 654 (1894).

<sup>33</sup> Bamberger, *Ber.*, **28**, 820 (1896).

the sodium salt of p-nitroisodiazobenzene is dissolved in cold, sixty per cent sulfuric acid. In principle the diazo compound undergoes hydrolysis as represented by the equation,



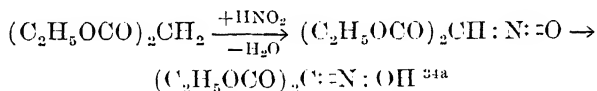
3. Hantzsch<sup>34</sup> reports the hydrolysis of the methyl ester of p-brom-diazobenzene to p-bromaniline and methyl aquonitrite,



Since nitrous acid is used in the preparation of these diazo compounds and is recovered when they are hydrolyzed, it is reasonable to conclude that one of the nitrogen atoms in the diazo group behaves as if it were nitrous acid nitrogen, the other as ammonia nitrogen.

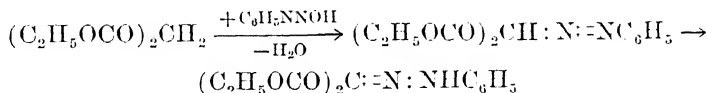
**Further Reactions of Diazobenzene.** A few reactions selected from the very large number into which the diazo compounds are known to enter are discussed briefly under this heading with the object in view of further substantiating Stieglitz' claim that the diazo compounds are derivatives of nitrous acid.

1. Nitrous acid acts on diethyl malonate as represented by the scheme,



to form the oxime of diethyl mesoxalate. In effect a methylene group is augmented to a ketone group, while at the same time nitrous acid is reduced to hydroxylamine.<sup>35</sup>

In a closely similar manner diazobenzene acts on diethylmalonate to form a phenylhydrazone of diethyl mesoxalate.<sup>36</sup> The equation,



represents the phenylhydrazone of diethyl mesoxalate as being formed by the same intramolecular augmentation and reduction re-

<sup>34</sup> Hantzsch, *Ber.*, **36**, 3097 (1903).

<sup>34a</sup> It will be recalled that colons are used to represent unions concerning which no assumptions are made.

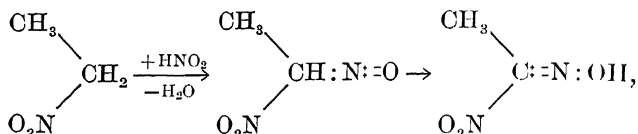
<sup>35</sup> Conrad and Bischoff, *Ann. Chem.*, **209**, 211 (1881); v. Meyer and Müller, *Ber.*, **16**, 608 (1883); Goldschmidt, *Ber.*, **16**, 1621 (1883).

<sup>36</sup> Elbers, *Ann. Chem.*, **227**, 355 (1885); R. Meyer, *Ber.*, **24**, 1241 (1891).

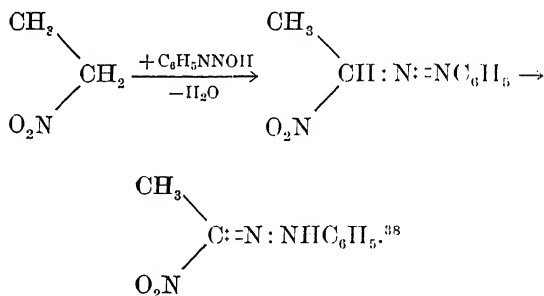
actions as those involved above, excepting that here a phenyl aqua-ammonio nitrous acid is reduced to phenylhydrazine, whereas above nitrous acid is reduced to hydroxylamine.

The much-discussed question as to whether in the first case a nitroso or an isonitroso compound is formed and in the second an azo compound or a phenylhydrazone need not concern us here though it may be said in passing that the well-known tendency of nitrous acid to act as an augmenting agent toward many compounds of carbon supports the conclusion that the compounds formed are respectively an oxime and a phenylhydrazone. It suffices present purposes to have shown the striking similarity in the behavior of nitrous acid on the one hand and of the diazo compounds on the other toward a class of compounds of which diethyl malonate is an example.

2. The reactions involved in the action of nitrous acid and diazobenzene respectively on the aliphatic nitro compounds are very similar. Nitroethane for example reacts with nitrous acid,



to form ethylnitrolic acid,<sup>37</sup> and with diazobenzene to form a compound which has been named benzeneazonitroethane,



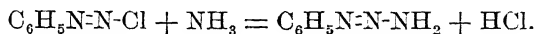
In the one case a nitroso group, second formula in the first equation, is reduced to a hydroxylamine group, in the other a near nitrogen analog of the nitroso group, contained in the second formula of the second equation, is reduced to a phenylhydrazine residue, while in both cases the  $\text{CH}_2$  group undergoes augmentation to the  $\text{CH}$  group.

<sup>37</sup> v. Meyer, *Ann. Chem.*, 175, 98 (1875).

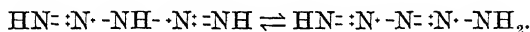
<sup>38</sup> Hantzsch and Kissel, *Ber.*, 32, 3146 (1899).

The close similarity in the behavior of nitrous acid and diazobenzene is here again exemplified.

3. Looking upon diazobenzene chloride as a mixed ester-chloride of nitrous acid one might expect it to be capable of undergoing ammonolysis in accordance with the equation,



This particular reaction is not known to take place. Instead of diazobenzeneamide a very unstable compound represented by the formula,  $\text{C}_6\text{H}_5\text{N}=\text{N}-\text{NH}-\text{N}=\text{NC}_6\text{H}_5$ , and known as bisdiazobenzeneamide is obtained by the action of ammonia on diazobenzene chloride.<sup>39</sup> It may be said of this compound that it is a diphenyl ester of an hypothetical ammono dinitrous acid,



*Metallic Salts.* Finally in agreement with the view that normal diazobenzene, isodiazobenzene and diazobenzeneamide are acid esters is the existence of the potassium and silver,  $\text{C}_6\text{H}_5\text{ON}_2\text{Ag}$ , salts of normal diazobenzene, of the potassium,  $\text{C}_6\text{H}_5\text{ON}_2\text{K}$ , sodium,  $\text{C}_6\text{H}_5\text{ON}_2\text{Na}$ , silver,  $\text{C}_6\text{H}_5\text{ON}_2\text{Ag}$ , and mercuric,  $(\text{C}_6\text{H}_5\text{ON}_2)_2\text{Hg}$ , salts of isodiazobenzene and of the cuprous  $\text{C}_6\text{H}_5\text{N}_3\text{Cu}$ , salt of diazobenzeneamide may be noted. Dimroth<sup>40</sup> had in his hands the silver salt of diazobenzeneamide but did not analyze it.

*Diazoaminobenzene.* Looked upon as a diphenyl ester of tri-basic ammono nitrous acid diazoaminobenzene should show acid properties which as a matter of fact it does. In liquid ammonia solution it conducts the electric current<sup>41</sup> and reacts with certain metallic amides to form salts.<sup>42</sup> The sodium,  $\text{C}_6\text{H}_5\text{N}=\text{N}(\text{Na})\text{C}_6\text{H}_5$ , silver,  $\text{C}_{12}\text{H}_{10}\text{N}_3\text{Ag}$ , cuprous,  $\text{C}_{12}\text{H}_{10}\text{N}_3\text{Cu}$ , cupric,  $(\text{C}_{12}\text{H}_{10}\text{N}_3)_2\text{Cu}$ , and mercuric salts are recorded in the chemical literature. A magnesium salt of the formula,  $\text{C}_6\text{H}_5\text{N}=\text{N}(\text{MgI})\text{C}_6\text{H}_5$ , has also been prepared. 4-4'-Dinitrodiazoaminobenzene is an acid of sufficient strength to decompose alkali carbonates.<sup>43</sup>

For the rest we must content ourselves here with a general statement to the effect that the methods of preparation and the many reactions into which diazoaminobenzene has been observed to enter are entirely in harmony with the assumption that it is an N·N'-diphenyl ammononitrite.

<sup>39</sup> v. Pechmann and Frobenius, *Ber.*, 27, 898 (1894); 28, 171 (1896).

<sup>40</sup> Dimroth, *Ber.*, 40, 2376 (1907).

<sup>41</sup> Griswold, Thesis, Stanford University, 1926.

<sup>42</sup> Fernelius, Thesis, Stanford University, 1926.

<sup>43</sup> Meldola and Streetfield, *J. Chem. Soc.*, 51, 445 (1887).

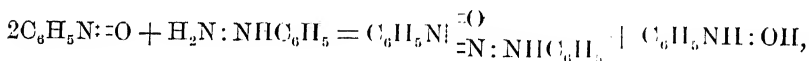
Derivatives of an Hypothetical Aquo-Ammono Nitrous Acid of the Formula,  $\text{HN} \begin{smallmatrix} \text{:O} \\ \text{---} \\ \text{:NH} \end{smallmatrix} \rightleftharpoons \text{HN} \begin{smallmatrix} \text{:OH} \\ \text{---} \\ \text{:N} \end{smallmatrix}$ . Aquo nitrous acid is usually regarded as a tautomeric compound to which either of the formulas,  $\text{HONO}$  or  $\text{HNO}_2$  are ascribed, while methyl nitrite and nitromethane are isomers represented respectively by the formulas,  $\text{CH}_3\text{ONO}$  and  $\text{CH}_3\text{NO}_2$ . Assuming that those properties of aquo nitrous acid which determine the existence of isomers such as methyl nitrite and nitromethane also inhere in the aquo-ammono acid it follows that it is reasonable to expect that derivatives of aquo-ammono nitrous acid represented by the above formulas may be found recorded in the literature.

In agreement with these speculations is Angeli's establishment of the formula,  $\text{C}_6\text{H}_5\text{N} \begin{smallmatrix} \text{O} \\ \text{=O} \\ \text{=NC}_6\text{H}_5 \end{smallmatrix}$ , for azoxybenzene and his conten-

tion that normal diazobenzene has the structure,  $\text{C}_6\text{H}_5\text{N} \begin{smallmatrix} \text{O} \\ \text{=O} \\ \text{=NH} \end{smallmatrix}$ .

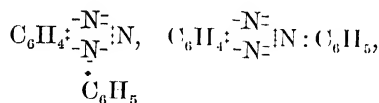
These two formulas represent nitrobenzene in which one of the oxygen atoms is replaced by the  $\text{NC}_6\text{H}_5$  group and the imide group respectively.

One might well conclude from its formation by the action of phenylhydrazine on nitrosobenzene as represented by the scheme,



that Bamberger's phenylazohydroxyanilide<sup>44</sup> is a phenylhydrazide of nitrobenzene, which in other words is to say a derivative of the tautomeric form of nitrous acid of the formula,  $\text{HNO}_2$ .

Representing 1-phenylbenzotriazol and 2-phenylbenzotriazol by the respective formulas,



it may be said that the first compound is a phenyl ester of an acid phenylene ammononitrite and that the second may be looked upon as nitrobenzene in which the two oxygen atoms are replaced by the phenylenediamine residue,  $\text{C}_6\text{H}_5\text{N}_2$ .

<sup>44</sup> Bamberger, *Ann. Chem.*, **420**, 167 (1919); *Helv. chim. Acta*, **14**, 254 (1931).

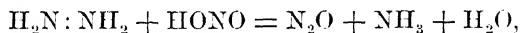
## CHAPTER XXXII.

### NITROUS ACID HYDRAZIDES AND OXIMES.

In further substantiation of the view that the diazo compounds are derivatives of nitrous acid nitrogen it is undertaken in this chapter to compare the behavior of aquo nitrous acid and the diazo compounds in respect to their action on hydrazine and hydroxylamine and their derivatives.

**Nitrous Acid and Hydrazine.** Assuming that the reactions involved in the action of diazo compounds on the hydrazines will be found to parallel more or less closely those which take place when nitrous acid acts on hydrazine it will be helpful in connection with our later discussion of some of these reactions to speculate here in some detail concerning the action of hydrazine on the three nitrous acids of the respective formulas,  $\text{HO} \cdot \text{N} \cdot \text{O}$ , known in solution and in the form of esters and salts,  $\text{H}_2\text{N} \cdot \text{N} \cdot \text{O} \rightleftharpoons \text{HN} \cdot \text{N} \cdot \text{OH}$ , and  $\text{H}_2\text{N} \cdot \text{N} \cdot \text{NH}$ , known in the form of esters and ester-salts.

It seems to be fairly well established<sup>1</sup> that two primary reactions are involved in the action of hydrazine on nitrous acid, the one, greatly predominating in the presence of weak acids, yields nitrous oxide, ammonia and water,



the other, which is favored by the presence of strong acids, gives hydrazoic acid and water,  $\text{H}_2\text{N} \cdot \text{NH}_2 + \text{HONO} = \text{HN} \cdot \text{N} \cdot \text{N} + 2\text{H}_2\text{O}$ .<sup>2</sup>

Having shown that hydrazoic acid is fairly certainly a tautomeric compound to which either of the formulas,  $\text{HN} \cdot \text{N} \cdot \text{N}$  or  $\text{HN} \cdot \underset{\text{N}}{\text{N}}$ ,<sup>3</sup>

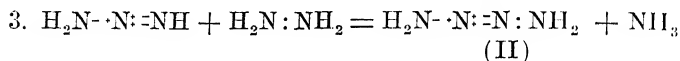
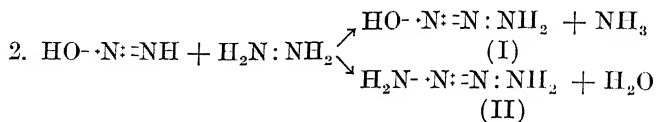
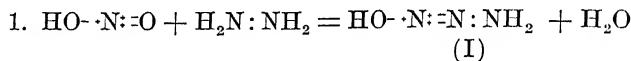
may be ascribed, and recalling that we have adopted the symbols,

<sup>1</sup> Sommer, *Z. anorg. Chem.*, **83**, 119 (1913); Sommer and Pincas, *Ber.*, **49**, 259 (1916).

<sup>2</sup> Nitrogen, which also appears among the products of the interaction of nitrous acid and hydrazine in strong acid solution, is formed along with nitrous oxide as the result of a reaction taking place between hydrazoic acid and nitrous acid. Sommer [*Ber.*, **48**, 1834 (1915)] writes the equations,  $\text{N}_2 \cdot \text{NH} + \text{HO} \cdot \text{NO} = \text{N}_2 \cdot \text{N} \cdot \text{NO} + \text{H}_2\text{O}$ , and  $\text{N}_2 \cdot \text{N} \cdot \text{NO} = \text{N}_2 + \text{N}_2\text{O}$ , to represent the reactions involved. This hypothetical compound,  $\text{N}_2 \cdot \text{N} \cdot \text{NO}$ , containing one nitric acid nitrogen atom, one nitrous acid nitrogen atom, two ammonia nitrogen atoms and one water oxygen atom, decomposes to form nitrous anammonide (nitrogen) and nitric anhydride-anammonide (nitrous oxide).

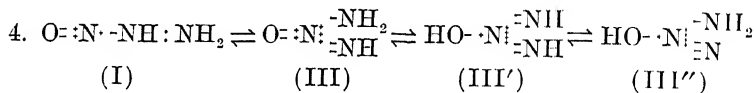
<sup>3</sup> It will be recalled (Chapter XIV) that hydrazoic acid may even be looked upon as a cyclic ammono hyponitrous acid.

$\cdot\text{N}\cdot$ ,  $\text{N}\cdot$ ,  $\cdot\text{N}:\text{N}\cdot$  and  $\text{N}\cdot$ , to represent nitric acid nitrogen, nitrous acid nitrogen hydrazine nitrogen and ammonia nitrogen respectively, we may reasonably speculate as follows concerning the action of hydrazine on the three nitrous acids. It is assumed that the primary reactions involved in the action of hydrazine on the respective acids take place in accordance with the equations,



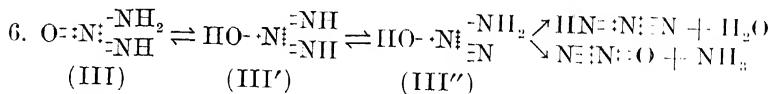
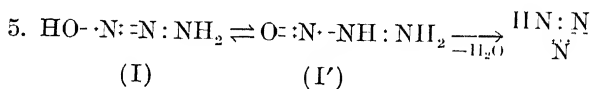
forming in the first case the nitrous acid hydrazide (I), in the third, the nitrous acid hydrazide (II), in the second either (I) or (II), depending upon whether water or ammonia is eliminated.

As represented by the equation,



it is further assumed that the nitrous acid hydrazide represented by formula (I), by intramolecular augmentation and reduction,<sup>5</sup> is transformed into an aquo-ammono nitric acid, (III) (III') (III''), which, together with the nitrous acid hydrazide (I) exists in tautomeric equilibrium.<sup>6</sup>

Assuming finally that these hypothetical tautomers may lose water or ammonia as represented by the schemes,

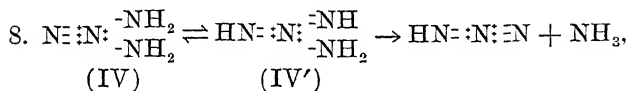
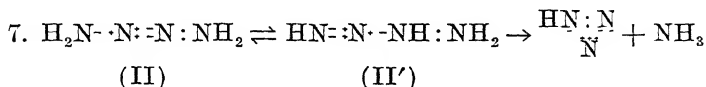


<sup>5</sup> It may be noted that the rearrangement of (I) into (III) (III') (III'') involves the augmentation of nitrous acid nitrogen to nitric acid nitrogen and the concomitant reduction of hydrazine nitrogen to ammonia nitrogen.

<sup>6</sup> Our earlier conclusion to the effect that hydrazoic acid is a tautomeric compound is taken to justify these assumptions.

we find hydrazoic acid appearing as a cyclic nitrous acid hydrazide and as an ammono nitric acid; nitrous oxide as a nitric anhydride anammonide.<sup>7</sup>

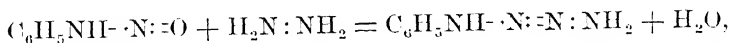
In a similar manner the second nitrous acid hydrazide (II), acting as such or as an ammono nitric acid (IV) (IV'), is assumed to be capable of breaking down to form hydrazoic acid and ammonia as represented by the equations,



hydrazoic acid again appearing as a cyclic nitrous acid hydrazide and as an ammono nitric acid.

The only justification for these speculations as to the manner in which the three nitrous acids react with hydrazine is that they put us in a position which enables us to explain in a very satisfactory manner the many reactions which have been observed to take place between nitrous acid and certain derivatives of hydrazine on the one hand and those which are involved in the action of diazo compounds on hydrazine and its derivatives on the other. It will appear as we proceed that in their reactions with derivatives of hydrazine, nitrous acid and the diazo compounds behave in a strikingly similar manner.

**Diazobenzene and Hydrazine.** When hydrazine hydrate is added to a cold solution of diazobenzene sulfate a practically quantitative yield of phenylazide is obtained. In strongly alkaline solution, in addition to phenylazide and ammonia, considerable quantities of hydrazoic acid and aniline are formed.<sup>8</sup> In explanation of these observations it may be assumed that in accordance with the equation,



a phenyl nitrous acid hydrazide is formed which, as such or as a phenyl ammononitrate, decomposes into phenylazide and ammonia and into hydrazoic acid and aniline in a manner which will be clear from a comparison of the scheme,

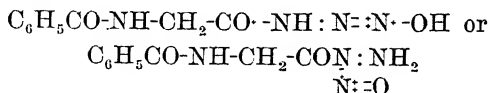
<sup>7</sup> Since the formal loss of ammonia on the part of tautomer (I) would involve the conversion of a nitrous acid hydrazide into a cyclic nitrous acid oxime, it is arbitrarily assumed that such a reaction does not take place.

<sup>8</sup> Curtius, *Ber.*, 26, 1267 (1893); Noeltig and Michel, *Ber.*, 26, 88 (1893).



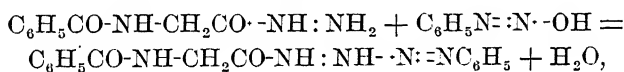


yield of a crystalline compound, which, though not satisfactorily analyzed, was very probably a mixed hippuric acid nitrous acid hydrazide of the formula,



When this compound was heated with acid or alkali solution hippuric acid and hydrazoic acid were formed; the reactions involved undoubtedly following the one or the other of the courses represented on page 301 for the decomposition of an hypothetical nitrous acid hydrazide.

**Diazobenzene and Hippurylhydrazide.** By the interaction of benzenediazonium sulfate and hippurylhydrazide in ice cold water Curtius<sup>14</sup> obtained a compound which he formulated as follows,  $\text{C}_6\text{H}_5\text{CO-NH-CH}_2\text{CO-NH-NH-N=N-C}_6\text{H}_5$ , and to which, on the basis of a supposed analogy between the hydrocarbon chain  $\text{CH}_3\text{CH}_2\text{-CH-CH}_2$  and the nitrogen chain,  $\text{H}_2\text{N-NH-N-NH}$ , he gave the name hippurylphenylbuzylene. The compound is clearly a mixed hydrazide of hippuric acid and a phenylnitrous acid as shown by its formation by the interaction of hippurylhydrazide and diazobenzene,



and by its ready decomposition in accordance with the equations 7 and 8, p. 303 to form phenylazide and hippuric amide on the one hand and aniline and hippuric acid azide on the other.

Many other examples might be given which would further emphasize the remarkably close resemblance between nitrous acid and the diazo compounds in respect to the reactions they undergo with hydrazine and its derivatives.

**The Action of Hydroxylamine and of Phenylhydroxylamine on Nitrous Acid and on Diazobenzene.** Without entering upon any extended speculations concerning the mechanisms of the reactions involved, which in a general way may be assumed to resemble those discussed at the beginning of this chapter, we content ourselves here with a brief summary of the interactions of nitrous acid and hydroxylamine, of diazobenzene and hydroxylamine, of nitrous acid and phenylhydroxylamine and of diazobenzene and phenylhydroxylamine. It will appear that nitrous acid and diazobenzene strikingly resemble each other in their behavior toward hydroxylamine and phenylhydroxylamine.

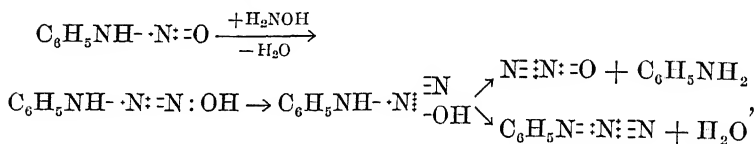
<sup>14</sup> Curtius, *Ber.*, 25, 1267 (1893).

*Nitrous Acid and Hydroxylamine.* Nitrous acid acts on hydroxylamine to form, for the most part, nitrous oxide and water,



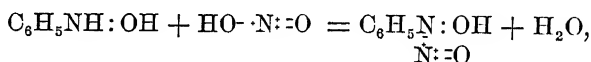
*Diazobenzene and Hydroxylamine.* Nitrous oxide and aniline, phenylazide and water have been obtained by the interaction of diazobenzene and hydroxylamine.<sup>15</sup>

Writing the scheme,



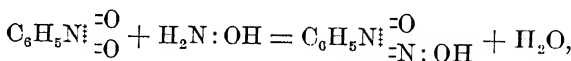
to represent the reactions involved it may be said that a phenyl nitrous acid oxime, formed by the action of hydroxylamine on diazobenzene, decomposes by way of a phenyl aquo-ammonio-nitrate to yield the four products formulated above.<sup>16</sup>

*Nitrous Acid and Phenylhydroxylamine.* Nitrous acid acts on phenylhydroxylamine, it may be assumed, as represented by the equation,



to give a practically quantitative yield of phenylnitrosohydroxylamine,<sup>17</sup> a fairly stable compound, which may be looked upon as an N-phenylhydroxylamine and at the same time a nitrous acid oxime.

The same compound has been obtained by the action of hydroxylamine on nitrobenzene,<sup>18</sup>



a method of preparation which Angeli interpreted as consisting in the formation of an oxime of nitrobenzene. Apparently the two formulas represent tautomers of one and the same compound.

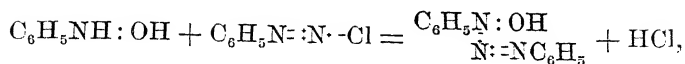
*Diazobenzene and Phenylhydroxylamine.* In a similar manner diazobenzene in hydrochloric acid solution reacts with phenylhydroxylamine in accordance with the equation,

<sup>15</sup> E. Fischer, *Ann. Chem.*, 190 (1878); Mai, *Ber.*, 25, 372 (1892).

<sup>16</sup> Cf. equations, 5, 6, p. 302 and 7, 8, p. 303. It is interesting to recall that the same four compounds are obtained when the unstable phenylnitrosohydrazine undergoes decomposition (p. 304).

<sup>17</sup> Wohl, *Ber.*, 27, 1436 (1894); Bamberger, *Ber.*, 27, 1553 (1894).

<sup>18</sup> Angeli, *Ber.*, 29, 1884 (1896).



forming a compound which is to be regarded as phenylnitrosohydroxylamine in which the nitrous acid group,  $\cdot\text{N}::\text{O}$ , is replaced by the phenylnitrous acid group,  $\cdot\text{N}::\text{NC}_6\text{H}_5$ . It may be said that the compound is at the same time a phenylhydroxylamine, a nitrous acid oxime and a nitrous acid phenyl ester.

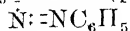
The same compound has been prepared by the interaction of nitrosobenzene and phenylhydrazine and named phenylazohydroxyanilide by Bamberger.<sup>19</sup>

The object aimed at in the preceding discussion has been to emphasize the close parallelism which exists between nitrous acid and diazobenzene in their behavior toward hydrazine and hydroxylamine and their derivatives thereby bringing support to our assumption that the same nitrous acid or tripositive nitrogen is present in both nitrous acid and diazobenzene and that the second nitrogen atom present in the latter compound is ammonia or trinegative nitrogen which functions in diazobenzene as water or dinegative oxygen does in nitrous acid. The speculations concerning the mechanisms of the reactions discussed are of minor importance though in the writer's opinion perhaps worth while.

### NITROGEN CHAINS

**Two Nitrogen Atoms.** The unknown diimide,  $\text{HN}::\text{NH}$ , hydrazine,  $\text{H}_2\text{N}::\text{NH}_2$ , and hyponitrous acid,  $\text{HON}::\text{NOH}$ , together with their derivatives contain two nitrogen atom chains.

**Three Nitrogen Atoms.** Triazene, which is an unknown ammono nitrous acid,  $\text{HN}::\text{N}\cdot\text{-NH}_2$ , and its derivatives such as diazobenzeneamide,  $\text{C}_6\text{H}_5\text{N}::\text{N}\cdot\text{-NH}_2$ , and diazoaminobenzene,  $\text{C}_6\text{H}_5\text{N}::\text{N}\cdot\text{-NHC}_6\text{H}_5$ , contain three nitrogen atom chains as do also certain derivatives of the purely hypothetical nitrous acid hydrazide,  $\text{HO}\cdot\text{-N}::\text{N}::\text{NH}_2$ , and the nitrous acid oxime,  $\text{H}_2\text{N}\cdot\text{-N}::\text{N}::\text{OH}$ , such for example as the nitrous acid phenylhydrazide,  $\text{C}_6\text{H}_5\text{NH}::\text{N}::\text{N}\cdot\text{-OH}$  (p. 304, this chapter), and so-called phenylazohydroxyanilide,  $\text{C}_6\text{H}_5\text{N}::\text{OH}$  (p. 307, this chapter), which may be regarded as a

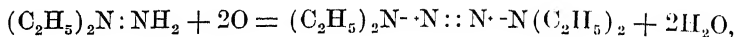


phenyl ammono nitrous acid derivative of phenylhydroxylamine. Phenylazide, whether looked upon as a straight chain or a cyclic compound, contains a chain of three nitrogen atoms.

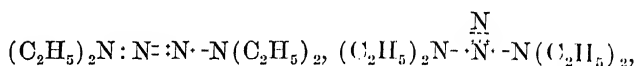
**Four Nitrogen Atoms.** Compounds containing chains of four ni-

<sup>19</sup> Bamberger, *Ber.*, **29**, 104 (1896), **33**, 3509 (1900); *Ann. Chem.*, **420**, 153 (1920); *Helv. Chim. Acta*, **14**, 242 (1931); Bamberger and Stiegelmann, *Ber.*, **32**, 3554 (1899); Bamberger and Rising, *Ann. Chem.*, **316**, 267, 271 (1901).

trogen atoms are certain nitrous acid hydrazides already discussed, among them Curtius' hippurylphenylbuzylene,  $\text{C}_6\text{H}_5\text{CONH}\cdot\text{CH}_2\text{CONH}\cdot\text{N}::\text{N}\cdot\text{NHC}_6\text{H}_5$  (p. 305, this chapter), and the tetrazenes, known also as tetrazones, which are obtained by oxidizing unsymmetrical dialkyl and diaryl hydrazines.<sup>19a</sup> Tetraethyltetrazene, for example, is formed by the action of mercuric oxide on  $\alpha$ -diethylhydrazine.<sup>20</sup> Writing the equation,

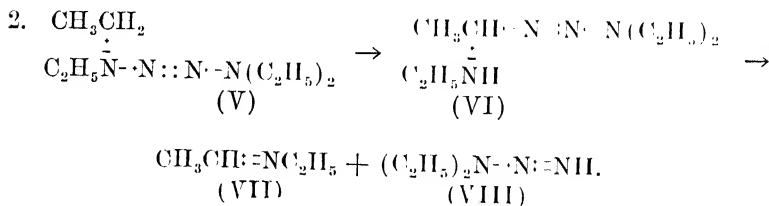
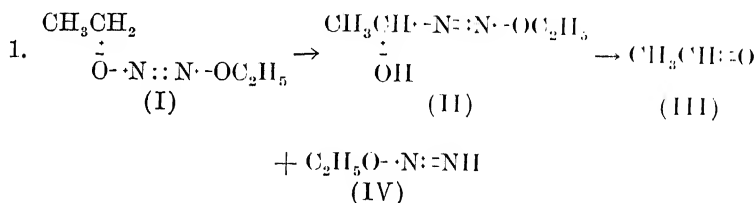


to represent what takes place the reaction involved may be said to consist in the oxidation of diethylhydrazine to a tetraethyl ester of an ammono hyponitrous acid. Tetraethyltetrazene may perhaps just as well be given the tautomeric formulas,



which represent the compound as a diethylhydrazide of a diethyl-nitrous acid and a tetraethyl ammononitrate respectively.

In harmony with the view that tetraethyltetrazene is an ester of an ammono hyponitrous acid, is the parallelism which exists between the decomposition this compound undergoes when warmed with dilute hydrochloric acid and that which takes place on warming diethyl aquohyponitrite with water. In the latter case ethyl alcohol, acetaldehyde and nitrogen are formed, in the former diethylamine, ethylamine, acetaldehyde and nitrogen. A way of explaining these results is summarized in the parallel schemes,

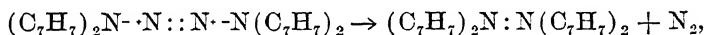


<sup>19a</sup> E. Fischer, *Ann. Chem.*, **190**, 167 (1877); Wieland, *Ber.*, **41**, 3498 (1908).  
<sup>20</sup> E. Fischer, *Ann. Chem.*, **199**, 319 (1879).

The aquo hyponitrous acid ester (I), undergoing a Beckmann-like rearrangement, passes over into the acetaldehyde-acetal, (II). This compound, decomposing after the familiar manner of the half-acetals, yields acetaldehyde, (III), and the nitrous acid ester, (IV), which latter unknown compound loses nitrogen (nitrous ammonide) to form ethyl alcohol. The second scheme represents a tetraethyl ammonohyponitrite as undergoing a closely similar rearrangement into the acetal (VI) which breaks down to form (VII) and (VIII). The aldehyde-ether (VII) hydrolyzes to acetaldehyde and ethylamine, the unknown nitrous acid ester, (VIII), decomposes to form diethylamine and nitrogen. In each case the assumed rearrangements involve, in principle, the augmentation of an alcohol to an aldehyde and the concomitant reduction of a hyponitrous acid to a nitrous acid.<sup>22</sup>

Benzyl hyponitrite decomposes in a similar manner to form benzyl alcohol, benzaldehyde and nitrogen.<sup>23</sup>

It is interesting to note that p-tetratolyltetrazene containing no augmentable alcohol group cannot rearrange as tetraethyltetrazene has been assumed to do. When heated in xylene solution it breaks down to form tetratolyldiazine and nitrogen,<sup>24</sup>



the two end ammonia nitrogen atoms undergoing augmentation to hydrazine nitrogen the middle hyponitrous nitrogen atoms reduction to elementary nitrogen.

**Five Nitrogen Atoms.** The compound represented by the formula,  $(\text{C}_6\text{H}_5\text{N}=\text{N})_2\text{NC}_6\text{H}_5$ , and known as bis-benzenediazoaniline, contains in its molecule a chain of five nitrogen atoms. It may be looked upon as a triphenyl ester of an hypothetical aquo-ammonio nitrous acid of the formula,  $\text{HN}::\text{N} \cdot \text{NH} \cdot \text{N}::\text{NH}$ . Hantzsch's<sup>25</sup> p-nitrobenzenediazoniumazide when represented by the formula,  $\text{NO}_2\text{C}_6\text{H}_4\text{N}::\text{N} \cdot \text{N}::\text{N}::\text{N}$ , contains a chain of five nitrogen atoms.

**Six Nitrogen Atoms.** An example of a compound containing a chain of six nitrogen atoms,  $\text{N}_4\text{HCN} \cdot \text{N}=\text{NH} \cdot \text{NH} \cdot \text{N}=\text{NCHN}_4$ , known as bis-diazotetrazolhydrazide, has been prepared by the action of hydrazine on diazotetrazole.<sup>26</sup> The reaction presumably takes place in accordance with the equation,

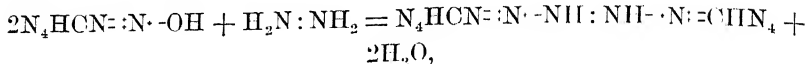
<sup>22</sup> Zorn, *Ber.*, 11, 1633 (1878); E. Fischer, *Ber.*, 11, 2210 (1878); *Ann. Chem.*, 199, 324 (1879).

<sup>23</sup> Hantzsch and Kaufmann, *Ann. Chem.*, 292, 329 (1896).

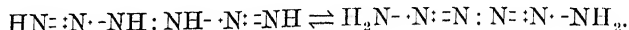
<sup>24</sup> Wieland, *Ber.*, 41, 3506 (1908).

<sup>25</sup> Hantzsch, *Ber.*, 36, 2056 (1903).

<sup>26</sup> Hofmann and Hock, *Ber.*, 44, 2953 (1911).

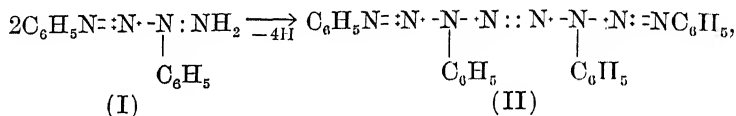


from which it appears that the compound is a ditetrazole derivative of an hypothetical nitrous acid hydrazide of the formula,



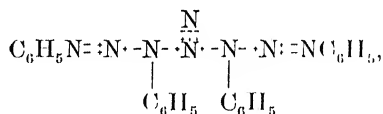
**Eight Nitrogen Atoms.** Compounds containing chains of seven nitrogen atoms are apparently unknown.

Bis-diazobenzenediphenyltetrazone, formed by the action of potassium permanganate on diazobenzenephnylhydrazide,



is an example of a compound containing a chain of eight nitrogen atoms.<sup>27</sup>

Assuming that the action of the potassium permanganate consists in the dehydrogenation of the hydrazine group contained in the diazobenzenephnylhydrazide (I) to an ammono hyponitrous acid group, as shown in (II), it becomes reasonable to say that Wohl and Schiff's compound is a tetraphenyl ester of an hypothetical mixed ammono nitrous ammono hyponitrous acid of the formula,  $\text{HN}::\text{N}\cdot\text{-NH}\cdot\text{-N}::\text{N}\cdot\text{-NH}\cdot\text{-N}::\text{NH}$ . Alternately this compound may be given the formula,



which represents a tetraphenyl ester of an ammono nitric ammono nitrous acid. This formula contains a chain of seven nitrogen atoms.

<sup>27</sup> Wohl and Schiff, *Ber.*, 33, 2741 (1900).

## CHAPTER XXXIII.

### AQUO-AMMONO SULFONIC ACIDS.

Ammono sulfonic acids, that is to say compounds represented by the formulas,  $RS(NH)_2NH_2$  or  $RS(N)NH$ , and therefore related to the aquo sulfonic acids as the acid amidines are related to the carboxylic acids, have never been prepared either in the free state or in the form of derivatives. However many compounds are known which may be regarded as mixed aquo-ammono sulfonic acids. For example, benzenesulfonamide and benzenesulfonimide, are aquo-ammono benzenesulfonic acids.

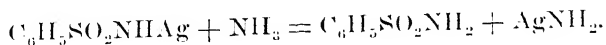
**Benzenesulfonamide, Aquo-Ammono Benzenesulfonic Acid,**  $C_6H_4SO_2NH_2$ . Benzenesulfonamide exhibits very distinctly the properties of an acid. In solution in liquid ammonia it discharges the red color of an alkaline solution of phenolphthalein, conducts electricity with facility, attacks the alkali metals, calcium, magnesium, and zinc with the evolution of hydrogen and reacts with ammono bases to form salts.<sup>1</sup>

**Metallic Salts.** Following is a list of metallic salts which have been prepared using liquid ammonia as solvent in which to accomplish the reactions involved. Excepting as otherwise indicated these salts are soluble in liquid ammonia and were obtained well crystallized.

*Monopotassium Aquo-Ammono-Benzenesulfonate.*  $C_6H_5SO_2NHK$ , is formed when solutions containing equimolecular amounts of benzenesulfonamide and potassium amide are brought together.

*Dipotassium Aquo-Ammono-Benzenesulfonate.*  $C_6H_5SO_2NK_2$ , is formed as a bulky, amorphous precipitate when benzenesulfonamide is added to an excess of potassium amide.

*Silver Aquo-Ammono-Benzenesulfonate.*  $C_6H_5SO_2NHAg$  and  $C_6H_5SO_2NHAg \cdot 2NH_3$ . The diammonated salt loses one molecule of ammonia in vacuum at laboratory temperature, the second molecule is expelled at  $120^\circ$ , the salt at the same time undergoing more or less ammonolysis in the manner represented by the equation,



Benzenesulfonamide silver was first obtained many years ago by

<sup>1</sup> Franklin and Kraus, *Am. Chem. J.*, 23, 292, 304 (1900); Franklin and Stafford, *Am. Chem. J.*, 28, 83 (1903); Franklin, *J. Am. Chem. Soc.*, 37, 2279 (1915).



adding silver nitrate in alcoholic ammonia solution to an alcohol solution of the acid amide.<sup>2</sup>

*Magnesium Aquo-Ammono-Benzenesulfonate*,  $(C_6H_5SO_2NH)_2Mg$  and  $(C_6H_5SO_2NH)_2Mg.xNH_3$ . This salt, containing an undetermined amount of ammonia of crystallization, has been obtained by the action of a solution benzenesulfonamide on metallic magnesium. The well formed crystals of the ammonated salt effloresce in vacuum at laboratory temperatures thus yielding the anammonous salt.

*Thallous Aquo-Ammono-Benzenesulfonate*,  $C_6H_5SO_2NHTl$ ,  $C_6H_5SO_2NHTl.NH_3$  and  $C_6H_5SO_2NHTl.2NH_3$ , is formed by dissolving thallous nitride in a solution of benzenesulfonamide. In vacuum the diammonate loses one molecule of ammonia at  $20^\circ$  and is completely deammonated at  $120^\circ$ .

*Cuprous Aquo-Ammono-Benzenesulfonate*,  $C_6H_5SO_2NHCu$  and  $C_6H_5SO_2NHCu.2NH_3$ . This salt is formed by dissolving ammonous cuprous nitride in a solution of benzenesulfonamide and allowing the solution to rest in contact with a piece of copper foil until it becomes nearly colorless. The ammonated salt loses its ammonia of crystallization at temperatures around  $160^\circ$ , at the same time undergoing a certain amount of ammonolytic decomposition. The salt is very susceptible to the action of atmospheric air, the least trace of which gaining entrance to the preparation tube brings about the formation of a blue layer on the surface of the solution.

*Cupric Aquo-Ammono-Benzenesulfonate*,  $(C_6H_5SO_2NH)_2Cu.4NH_3$  and  $(C_6H_5SO_2NH)_2Cu.7NH_3$ . The heptammonated salt is obtained in the form of intensely blue crystals by concentrating and cooling the solution formed by dissolving cupric oxide in a solution of the acid amide. In vacuum at laboratory temperature the heptammonate loses three molecules of ammonia. At higher temperatures the salt is converted into a mixture of the cuprous salt and free acid amide with the simultaneous evolution of nitrogen.

*Monopotassium Aquo-Ammono-m-Methoxybenzenesulfonate*,  $CH_3O-C_6H_4SO_2NHK$ .

*Dipotassium Aquo-Ammono-m-Methoxybenzenesulfonate*,  $CH_3O-C_6H_4SO_2NK_2$ , is formed as an amorphous precipitate on adding the acid amide to an excess of potassium amide in liquid ammonia solution.

*Potassium Aquo-Ammono-p-Methoxybenzenesulfonate*,  $CH_3O-C_6H_4SO_2NHK$ .

*Potassium Aquo-Ammono-p-Toluenesulfonate*,  $C_7H_7SO_2NHK$ , is formed as an amorphous precipitate when potassium amide is added to a solution of p-toluenesulfonamide.

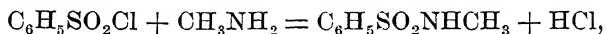
<sup>2</sup> Gerhardt and Chiozza, *Ann. Chem.*, **87**, 299 (1853).

*Thallous Aquo-Ammono-p-Toluenesulfonate*,  $C_7H_7SO_2NHTl$  and  $C_7H_7SO_2NHTl.NH_3$ . Dried at  $20^\circ$  the salt contains one molecule of ammonia which it loses at higher temperatures.

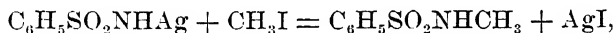
*Cuprous Aquo-Ammono-p-Toluenesulfonate*,  $C_7H_7SO_2NHCu.2NH_3$ .

*Cupric Aquo-Ammono-p-Toluenesulfonate*,  $(C_7H_7SO_2NH)_2Cu.xNH_3$ . When the precipitate formed by the action of potassium amide on cupric nitrate is dissolved in a solution of p-toluenesulfonamide a solution is formed from which the cuprous and the cupric salts were obtained, the one colorless the other intensely blue.

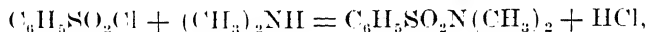
*Esters and Ester-Salts*. Alkyl derivatives of benzenesulfonamide and benzenesulfonimide have been prepared by methods involving reactions identical in principle with those familiarly concerned in the preparation of esters in general. Examples of such reactions are the following. The monomethyl ester of benzenesulfonamide is formed by the action of methylamine on benzenesulfonchloride,



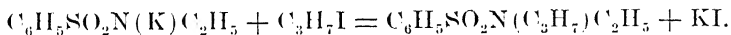
and also by the interaction of benzenesulfonamide silver and methyl iodide,



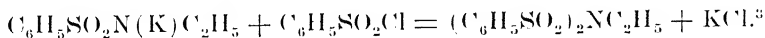
the dimethyl ester by the action of dimethylamine on benzenesulfonchloride,



the N-ethyl-N-propyl ester by the action of n-propyl iodide on the potassium salt of the monoethyl ester of benzenesulfonamide,



The ethyl ester of benzenesulfonimide has been obtained by the action of benzenesulfonchloride on N-ethylbenzenesulfonamide in the presence of alkali,



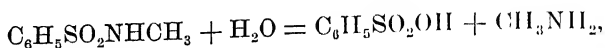
Ester-salts represented by the respective formulas,  $C_6H_5SO_2N(K)CH_3$ ,  $C_6H_5SO_2N(K)C_2H_5$ , and  $C_6H_5SO_2N(Na)C_2H_5$ ,<sup>4</sup> have been prepared though their existence was not confirmed by analysis.

<sup>3</sup> O-Alkyl and O-aryl esters of benzenesulfonamide have not been prepared.

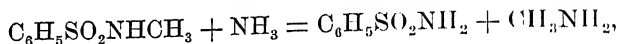
<sup>4</sup> Romburgh, *Rec. trav. chim.*, **3**, 16 (1884); Mulder, *Monatsh.*, **25**, 105 (1906); Kudernatsch, *Monatsh.*, **23**, 120 (1902).

However Marckwald<sup>5</sup> prepared and established the composition of the sodium salt of benzenesulfon-n-heptylamide,  $C_6H_5SO_2N(Na)C_7H_{15}$ .

All these compounds, which in accordance with the above considerations are to be looked upon as N-esters of aquo-ammono benzenesulfonic acids, undergo hydrolytic decomposition when heated with aqueous hydrochloric acid. The methyl ester of benzenesulfonamide, for example, is hydrolyzed as represented by the equation,



to aquo benzenesulfonic acid and methylamine which is an ammonio methyl alcohol. Whether or not this ester may be ammonolyzed in accordance with the equation,



has not been determined.

**Benzenesulfonnitramide**,  $C_6H_5SO_2NII-NO_2$ . As might well be expected of a derivative of ammonia in which two of the three ammonia hydrogen atoms are replaced by two strong acid-forming groups this aquo-ammono benzenesulfonic aquo-ammono nitric acid possesses the properties of a strong acid. In water solution it reddens litmus, attacks magnesium and zinc, dissolves carbonates with the evolution of carbon dioxide and is a good conductor of electricity. In liquid ammonia it discharges the red color of an alkaline solution of phenolphthalein, attacks magnesium and zinc and is an excellent conductor.

Hinsberg,<sup>6</sup> who first prepared benzenesulfonnitramide, was well aware of its acid properties but took the trouble to prepare the ammonium and potassium salts only.

In order to show that the number of possible salts of this acid is limited by the number of available bases, Mathews,<sup>7</sup> using water as solvent, prepared fourteen salts of the mixed acid. He also prepared nine salts of p-toluenesulfonnitramide and seven salts of o-nitro-p-toluenesulfonamide.

Eiskampf,<sup>8</sup> while failing to isolate the free acids, succeeded in preparing the ammonium  $C_{10}H_7SO_2NNO_2 \cdot NH_4$ , sodium  $(C_{10}H_7SO_2NNO_2)_2Na$ , potassium  $C_{10}H_7SO_2NNO_2K$ , calcium  $(C_{10}H_7SO_2NNO_2)_2Ca \cdot H_2O$ , barium  $(C_{10}H_7SO_2NNO_2)_2Ba \cdot 2H_2O$ , cupric  $(C_{10}H_7SO_2$

<sup>5</sup> Marckwald, *Ber.*, 32, 3513 (1899).

<sup>6</sup> Hinsberg, *Ber.*, 25, 1095 (1902).

<sup>7</sup> Mathews, *J. Phys. Chem.*, 24, 108 (1920).

<sup>8</sup> Marguerite Eiskampf, Thesis, Stanford University, 1921.

$\text{NNO}_2)_2\text{Cu}.4\text{NH}_3$ , silver  $\text{C}_{10}\text{H}_7\text{SO}_2\text{NNO}_2\text{Ag}$ , and nickel  $(\text{C}_{10}\text{H}_7\text{SO}_2\text{NNO}_2)_2\text{Ni}.6\text{NH}_3$ , salts of  $\beta$ -naphthalenesulfonnitramide and the ammonium  $\text{NO}_2\text{C}_{10}\text{H}_6\text{SO}_2\text{NNO}_2\text{NH}_4$ , sodium  $\text{NO}_2\text{C}_{10}\text{H}_6\text{SO}_2\text{NNO}_2\text{Na}$ , potassium  $\text{NO}_2\text{C}_{10}\text{H}_6\text{SO}_2\text{NNO}_2\text{K}$ , barium  $(\text{NO}_2\text{C}_{10}\text{H}_6\text{SO}_2\text{NNO}_2)_2\text{Ba}.2\text{H}_2\text{O}$ , cupric  $(\text{NO}_2\text{C}_{10}\text{H}_6\text{SO}_2\text{NNO}_2)_2\text{Cu}.5\text{NH}_3$ , silver  $\text{NO}_2\text{C}_{10}\text{H}_6\text{SO}_2\text{NNO}_2\text{Ag}$  and nickel  $(\text{NO}_2\text{C}_{10}\text{H}_6\text{SO}_2\text{NNO}_2)_2\text{Ni}.6\text{NH}_3$ , salts of a nitro- $\beta$ -naphthalenesulfonamide,  $\text{NO}_2\text{C}_{10}\text{H}_6\text{SO}_2\text{NH}\cdot\text{NO}_2$ .



## APPENDIX.

### MANIPULATION OF LIQUID AMMONIA.

Liquid ammonia may be conveniently removed from the commercial cylinders and transferred to vessels open to the atmosphere by following the procedure herewith described.

In Figure 5, *A* is a cylinder containing liquid ammonia. *E* is a convenient length of small lead tubing soldered at the one end to the steel fitting *D* and

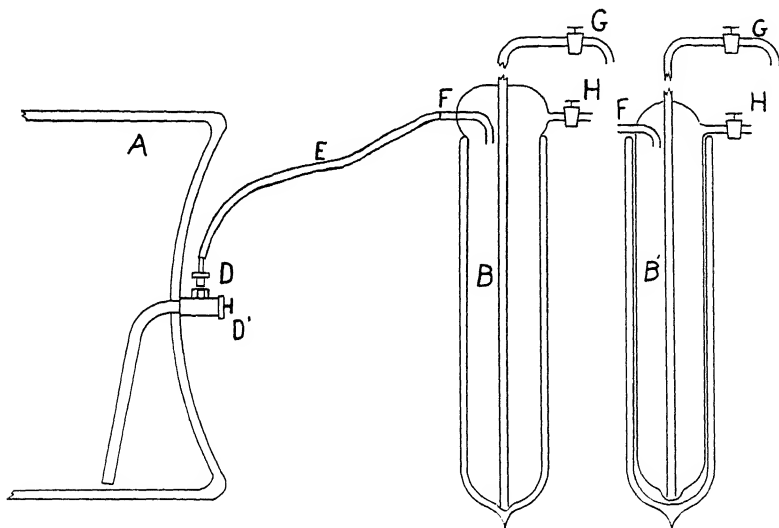


FIG. 5

attached at the other end to the ingress *F* of the vacuum-jacketed container *B* by means of a piece of heavy-walled rubber tubing securely wired on. In lieu of the vacuum-jacketed container *B* a plain one *B'* may be placed in a Dewar cylinder as shown in the figure. The exit *H* is connected with a large bottle, or carboy, half filled with water. The stopcock tube *G* is sealed to the vessel *B* at right angles to the plane of the figure. When, now, with stopcock *H* opened and *G* closed, the valve *D'* on the stock cylinder is carefully opened liquid ammonia, at its boiling point at atmospheric pressure, will collect in receptacle *B* while at the same time ammonia gas will find its way through stopcock *H* into the carboy of water where it will be absorbed.

In order to draw liquid from the container *B* into a vessel open to the atmosphere, stopcock *H* is closed and *G* is opened. Gas pressure on the surface of the liquid in *B* then forces the liquid out through *G* into the open. Following the procedure thus described liquid ammonia may easily and safely be removed from the commercial cylinders in any desired quantity.

Using vacuum-jacketed beakers, flasks and funnels, sketches of which are shown in Figure 6, the manipulation of liquid ammonia in open vessels becomes a comparatively simple matter provided the presence of more or less water is unobjectionable. For example Bohart<sup>1</sup> prepared pure potassium nickel cyanide

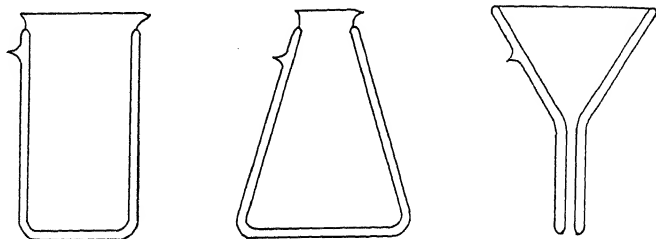


FIG. 6

by adding nickel sulfate to a liquid ammonia solution of potassium cyanide, filtering the solution of the soluble double cyanide, formed in accordance with the equation,  $\text{NiSO}_4 + 4\text{KCN} = 2\text{KCN.Ni(CN)}_2 + \text{K}_2\text{SO}_4$ , from the potassium sulfate and any potassium carbonate which may have been present in the potassium cyanide used, and removing the solvent from the solution of the double salt thus obtained by evaporation. Potassium cyanide and sodium cyanide have been purified by dissolving the salts in liquid ammonia, filtering off the insoluble carbonates and hydroxides and evaporating the solutions of the pure salts to dryness.

**Small Liquid Ammonia Containers.** For general laboratory purposes it is necessary to use small steel containers provided with well-made needle valves. Such containers may be of one to three or more liters capacity.

Liquid ammonia may be transferred from the large commercial cylinders to these small steel containers, by connecting the two cylinders by means of a lead tube provided with suitable fittings, as shown in Figure 7, opening valves *C*

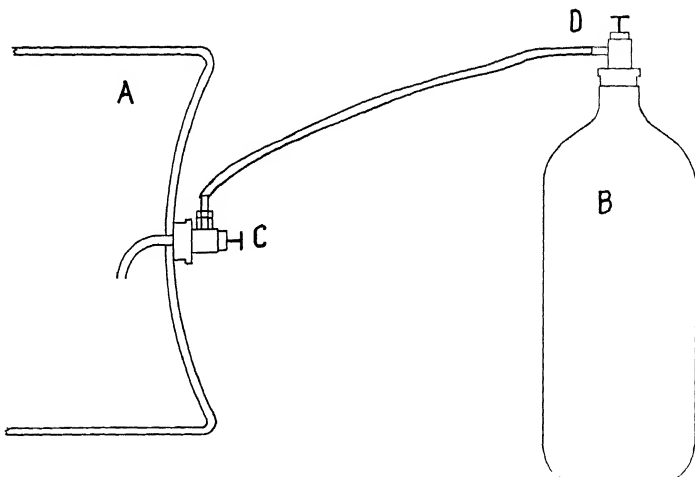


FIG. 7

<sup>1</sup> Bohart, *J. Phys. Chem.*, **19**, 546 (1914).

and *D* and then gently warming cylinder *A* or cooling *B*. Under the conditions thus described, provided *B* contains no atmospheric air or other permanent gas, liquid flows readily from *A* into *B*. With *B* tared and standing on a small platform scales the transfer of liquid is easily followed. Care must of course be taken not to fill the small cylinder completely.

If ammonia from the auxiliary cylinder is later to be withdrawn in the form of gas, the complete absence of water is assured by placing a few grams of metallic sodium in the cylinder *B* before charging it with liquid ammonia. The sodium, under the catalytic action of the cylinder walls, is rapidly converted into sodium amide which, like the metal itself, is an efficient drying agent.

**Reactions in Liquid Ammonia Contained in Closed Systems.** In general the reactions which have been studied in this laboratory have been carried out under conditions which insure all but absolute exclusion of water and atmospheric air in a manner which will be clear from descriptions of several typical procedures.

**Preparation of Silver Amide.**<sup>2</sup> This highly explosive compound is formed as a white precipitate when a liquid ammonia solution of potassium amide is poured into a similar solution of silver nitrate.

A detailed description of the manipulations involved in the preparation of these solutions, of washing the precipitate, determining its weight and removing it from the reaction tube for analysis, follows.

In Figure 8, *A* is a small steel cylinder containing dry liquid ammonia. *F G*

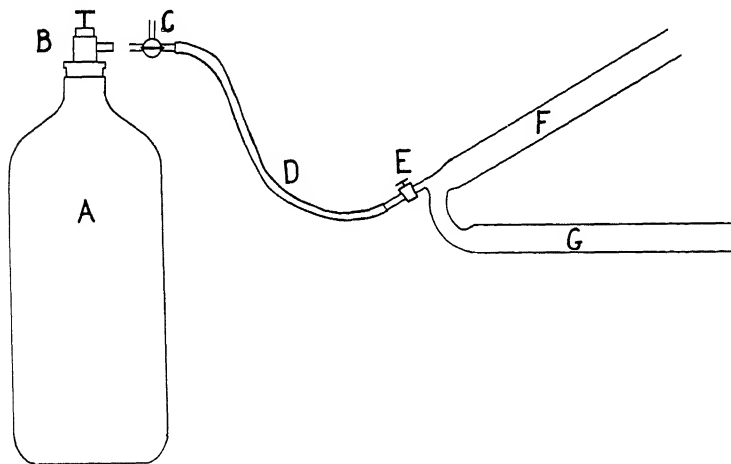


FIG. 8

is a two-legged reaction tube of about 1 mm. wall thickness, 15 to 20 mm. in diameter and with each leg some 15 to 20 cm. in length. *C* is a small 3-way stopcock, preferably of metal, attached to the exit of valve *B*, though it may be of glass in which case the connection is made to *B* by means of sealing wax. *D* is a lead tube of small diameter (2 to 4 mm.) the one end of which is soldered to *C*, the other attached to the reaction tube at *E* by means of sealing wax.

This set-up completed, one proceeds to dry the legs of the reaction tube. Leg *G* is closed by means of a cork stopper, stopcock *E* is opened and the three-way stopcock *C* is set to open the way from *B* through *D*, *E* and *F* to the outside.

<sup>2</sup> Franklin, *J. Am. Chem. Soc.*, **27**, 833 (1905).



*B* is then opened slightly and with a slow current of ammonia passing, leg *F* is dried by heating it gently with a Bunsen flame. Transferring the stopper from *G* to *F* the former leg is dried in a similar manner. After the reaction tube has cooled to the temperature of the laboratory and with ammonia gas streaming through leg *G* (*F* being closed) a known quantity of metallic potassium<sup>3</sup> is introduced into *G* and placed in a position well up toward the bend. For the purpose of catalyzing the action between the metal and liquid ammonia to form potassium amide a minute quantity of platinum black, contained in a long-handled platinum spoon, is first gently heated to remove moisture and then placed in *G* beside the metallic potassium. In general it is more convenient to use a small spiral of steel wire as catalyst. The spiral is placed in *G* near the exit, heated in the current of escaping ammonia to increase its catalytic activity and then pushed up the tube into the vicinity of the potassium by means of a glass rod. Leg *G* is now closed by sealing off the exit end, proceeding in detail as follows.

Simultaneously closing *G* by means of a cork stopper and setting the three-way stopcock *C* to connect *B* and the reaction tube to the atmosphere, the operator proceeds to seal off the end of *G* at a point well away from the cork stopper, using for the purpose a small hand blast lamp. Keeping the glass soft the closed end of *G* is blown into symmetrical shape by pressure brought about within the system by momentarily closing the opening at *C* by means of the left-hand forefinger. Before allowing the seal to cool the blast is played back a distance of several centimeters from the end of the tube in order to eliminate the sharp transition zone between the hot end and the adjacent cooler portions of the tube, otherwise the end of the tube will occasionally crack off spontaneously after a time.

Having thus finished with leg *G* one brings leg *F* into a horizontal position, as shown in Figure 10, establishes a current of ammonia through *F* by properly setting stopcock *C* and simultaneously removing the stopper from *F*. Following these operations a quantity of silver nitrate equivalent to the metallic potassium contained in *G*, is introduced into *F*, using for the purpose a long handled platinum spoon. Leg *F* is then closed after the manner already described for closing *G*. Stopcock *C* (Fig. 8) is now set to close communication with the atmosphere and at the same time valve *B* is closed.<sup>4</sup>

After leg *F* has cooled the metallic potassium and silver nitrate are brought into solution in liquid ammonia. To this end the reaction tube is immersed in an ice and water bath as shown in Figure 12. Then with a glass screen interposed between the apparatus and the operator,<sup>5</sup> ammonia is distilled from the steel cylinder *A*, Figure 8, into the reaction tube until each of the two legs is about one-third full whereupon with *E* and *B* (Fig. 8) closed and with *C* open to the air, the lead tube is unsealed from *E* by softening the sealing wax by means of a small flame.

<sup>3</sup> A measured length is cut from a glass tube which has been filled with metallic potassium in the following described manner. *A* in Figure 9 represents a clean dry tube of any convenient dimensions, constricted at (*a*) and containing a lump of potassium at (*b*). The tube, disposed in a perpendicular position, is attached to an air pump and exhausted following which it is heated either with a Bunsen flame or better by means of a long slender electrically heated air bath as shown in the figure. The metal melts and leaving all dross behind, runs down through the constriction (*a*) into the long narrow portion of the tube. Admitting ammonia gas to the upper portion of the tube forces the metal into the form of a continuous cylinder. The tube containing the clean potassium is now detached and closed with a rubber cap.

<sup>4</sup> When it happens to be desirable to avoid shortening the legs of the reaction tube unduly, the following alternative procedure for closing the tube is convenient. With the stopper closing one of the legs and with ammonia escaping through the other, the blowpipe flame is played simultaneously at a point near the tube exit and on the end of a glass rod as shown in Figure 11. When the glass has softened the rod is joined to the tube and bent into the position shown to serve as a handle while closing the tube. Just before the opening through the seal is entirely closed stopcock *C* is opened to the atmosphere, following which the seal is completed, as described above, and allowed to cool.

<sup>5</sup> In addition to using the glass screen the careful worker will further protect his eyes by wearing glasses or goggles.

Removing the reaction tube from the ice bath it is set aside until the metallic potassium, now in solution in liquid ammonia, is converted into the very soluble potassium amide under the catalytic action of the iron wire. During this action the stopcock *B* is opened slightly from time to time in order to avoid undue pressure within the tube as a result of the accumulation of hydrogen gas.

After the blue color of the potassium solution has completely disappeared and all the hydrogen has been allowed to escape, the reaction tube contains in the

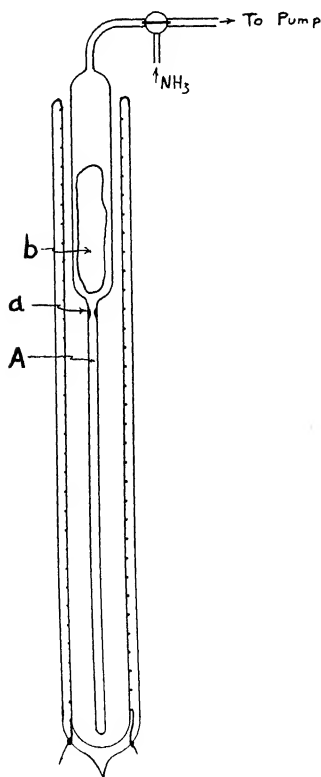


FIG. 9

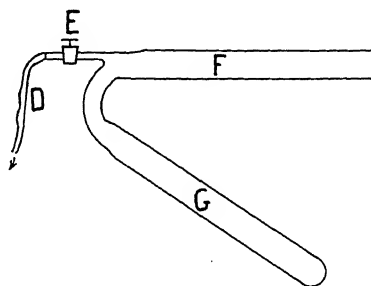


FIG. 10

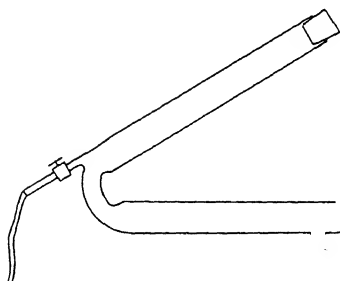


FIG. 11

one leg, *F*, a solution of silver nitrate, in the other, a solution of potassium amide together with the catalyst material and the piece of glass tubing introduced with the metallic potassium.

The reaction tube is now taken in the left hand—gloved it may be, though hardly necessary—and tipped in such a manner as to pour a portion of the potassium amide solution into the silver nitrate solution. When this is done a white, insoluble precipitate of silver amide is formed. Completely immersing the reaction tube—excepting of course the stopcock, which serves as a handle—in an ice-water bath brings about the condensation of ammonia on the inner walls of the reaction tube, thereby washing them clear of solution. After shaking the reaction tube to mix the contents of leg *F* and allowing the precipitate to settle, further successive portions of potassium amide solution are poured

into the solution of silver nitrate so long as the formation of a precipitate continues, or until all the potassium amide is used up.

While conducting the operations just described, as well as those involved in washing the precipitate, it is particularly necessary to keep the inner walls of the reaction tube wet with liquid ammonia, a condition which is maintained by completely immersing the reaction tube from time to time in an ice water bath. By keeping the walls of *F* wet one can, in general, keep them free from particles of the precipitate. In case such particles are allowed to become dry in contact with the tube walls, they cannot be detached and returned to the main body of the precipitate.

The washing of the precipitate is accomplished as follows. Allowing the precipitate to settle, the supernatant liquid, consisting essentially of a solution of

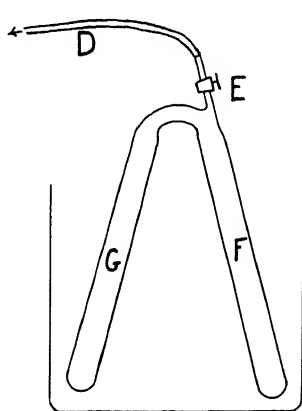


FIG. 12

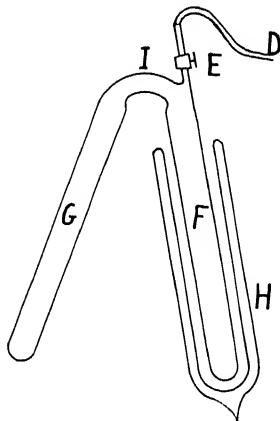


FIG. 13

potassium nitrate, is decanted from the precipitate into leg *G*. Placing leg *F* in an ice bath and *G* in tepid water the pure solvent distils rapidly over from the latter to the former leg of the reaction tube. The tube is then shaken to mix the contents of the leg *F*, or in lieu of this, leg *G* is placed in the ice bath and the lower end of *F* in tepid water with the result that the mixing is accomplished by the boiling of the liquid in the latter leg. The precipitate is allowed to settle and again the supernatant solution is decanted into leg *G*. This washing process is continued until all the soluble material is removed from the precipitate.

The two legs of the reaction tubes are now sealed apart in the following described manner. The leg *F*, containing the washed precipitate well covered with liquid ammonia, is placed in an ice bath, the stopcock is opened slightly and at the same time leg *G* is immersed in tepid water. With proper adjustment of the stopcock *E* the ammonia in *G* evaporates away without increasing or decreasing the amount of the liquid covering the silver amide. It is particularly important that the gaseous pressure on the surface of the liquid covering the precipitate be not unduly lowered since superheating of the liquid thereby brought about is apt to cause sudden violent boiling, or bumping, with the result that portions of the precipitate may be thrown up on the walls of the tube *F* and over into leg *G*, or even possibly plugging the outlet tube. After the solvent has disappeared from *G*, stopcock *E* is closed, leg *F* is transferred from the ice

bath to a bath of liquid ammonia contained in a Dewar vessel as shown in Figure 13, following which connection is made with the stock cylinder of liquid ammonia (*A* in Fig. 8). With stopcock *C* open to the atmosphere and to *D*, valve *B* is opened sufficiently to allow a slow stream of ammonia gas to escape through *C* to the atmosphere. Then removing the ammonia bath from leg *F*, the latter is slightly warmed by contact with the hand until the pressure within is raised slightly above that of the atmosphere. Stopcock *E* is then opened cautiously with the result that the air in the connecting lead tube is swept out through exit *C*. Closing *E*, the liquid ammonia bath is placed in its former position around leg *F*, after which *E* is opened wide. The continuous slow stream of gas from *B* out through *C* precludes any possible entrance of water vapor or oxygen from without while at the same time atmospheric pressure prevails within the reaction tube. Under these conditions leg *G* is easily detached from *F* by sealing off at *I*, using for the purpose the small hand blast lamp mentioned above. The stopcock *E*, which should be a well-ground one, is now closed, the lead tube is unsealed, and all the sealing wax is carefully removed from the stopcock-tube *E*. Small quantities of wax which, through inadvertence on the part of the operator, may have gained entrance to the exit tube of stopcock *E*, may be washed out by inserting the tip of a needle pointed pipette containing alcohol into the tube and forcing solvent through and out of the tube until all of the sealing wax is removed. Following the alcohol successively by ether and air the tube is easily dried. During these operations *F* is kept cold by immersing it in the liquid ammonia bath from time to time.

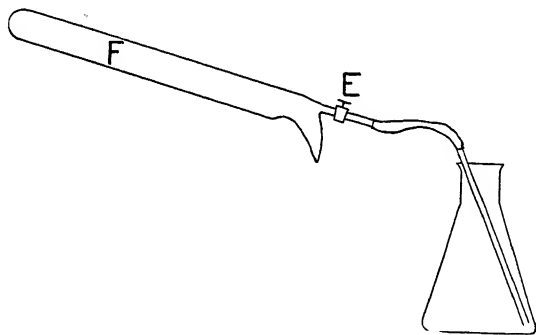


FIG. 14

The single-legged reaction tube *F* is now removed from the ammonia bath and connected to a Töpler pump by means of a piece of small rubber tubing securely wired on. The stopcock is opened sufficiently to allow the ammonia slowly to evaporate away through the pump. After the liquid has disappeared the stopcock is opened wide and the residual gas is completely removed by the action of the pump. The preparation tube, now containing nothing other than the pure silver amide, is detached from the pump and weighed.<sup>6</sup> The silver amide is then brought into water solution in the form of silver sulfate and ammonium sulfate, and removed from the preparation tube in the following manner.

The air in the exterior end of the stopcock-tube is displaced by water, using for the purpose a small, narrow-stemmed pipette. Connection of the preparation tube with a beaker of freshly boiled water is then made as represented in Figure 14, the connecting tube of glass and rubber being likewise filled with water.

Since liquid water on coming into contact with silver amide inevitably brings

<sup>6</sup> Because of its highly explosive character especial care must be exercised in handling this substance. [Cf. Franklin, *J. Am. Chem. Soc.*, **27**, 833 (1905)].

about an explosion, it is necessary to effect the hydrolysis of the amide by the action of water vapor. To this end, with the preparation tube held in the position shown in the figure, the stopcock is opened sufficiently to allow a small quantity of water to run into the lower end of the tube. The tube is now full of water vapor which in the course of some hours safely hydrolyzes the preparation. With the hydrolysis of the preparation completed, dilute sulfuric acid in amount somewhat more than necessary to neutralize the hydrolytic products is run into the tube in a manner which is obvious.

All that is now necessary in order to learn the composition of the preparation is to remove the aqueous solution of silver and ammonium salts from the preparation tube, determine quantitatively the silver and ammonia content and weigh the empty tube.

To empty the preparation tube of its contents it is connected with a 100 cc. flask and this in turn to a Bunsen pump as represented in Figure 15. After

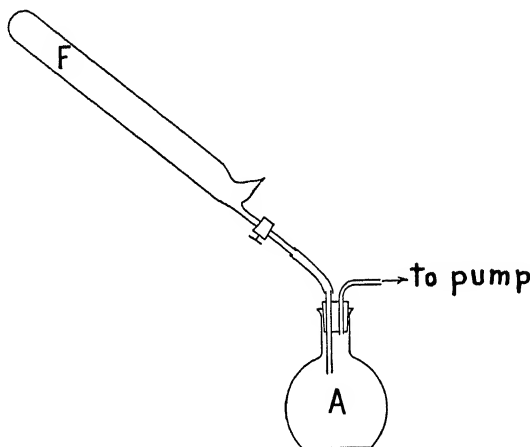


FIG. 15

setting the pump into action and opening the stopcock, a small bubble of air, which had been allowed to enter the tube after the completion of the hydrolytic decomposition of the silver amide, forces the solution from the tube *F* into flask *A*. Stopcock *E* is then closed, the pump tube is detached from flask *A*, followed by that of the preparation tube from the flask. The exit of the preparation tube is then immersed in a beaker of water and the stopcock opened sufficiently to allow a small quantity of water to enter, following which the operation described above is repeated to transfer this dilute solution to flask *A*. This rinsing process may be carried through once or twice again. Flask *A* is set aside for later quantitative determination of its silver and ammonia content.

The water remaining in the preparation tube is removed by rinsing out with alcohol, the alcohol in turn by repeated rinsing with dry air in the following detailed manner. With a pressure below that of the atmosphere established within the preparation tube, alcohol is run in by dipping the stopcock exit into a beaker of alcohol and cautiously opening stopcock. Connecting preparation tube to an empty flask as shown in Figure 15, the alcohol is removed by setting the pump in action and opening stopcock *E*. Then with the preparation tube distinctly warm the alcohol vapor is rinsed out with atmospheric air by alternately making and breaking its connection with the water pump. Finally with

the complete evacuation by means of the Töpler pump and weighing of the empty tube the weight of the preparation becomes known.

The weight of the preparation thus determined together with the amounts of silver and ammonia found in the aqueous solution of silver sulfate and ammonium sulfate obtained as described above, supply the data for calculating the composition of the silver compound found by the interaction of potassium amide and silver nitrate.

**Preparation of Lead Imide.**<sup>8</sup> In preparing silver amide as described above potassium amide solution was run into a solution of silver nitrate. To obtain lead imide, free from admixture of basic salt, by the interaction of potassium amide and lead iodide, it is necessary to reverse the order of mixing the reactants, that is to say, the lead iodide solution must be poured into a solution of potassium amide. To accomplish this end the procedure is as follows. A known amount of metallic potassium, together with the catalyst, is placed in leg *G* of the reaction tube set-up, as shown in Figure 8, following which the open ends of *F* and *G* are closed and ammonia is distilled into leg *G*, all after the manner already described. The reaction tube is then detached at *E* and set aside until the blue color of the potassium solution has disappeared.

The potassium amide solution thus formed is transferred to leg *F*, complete removal of solution being accomplished by rinsing *G* with successive small portions of solvent distilled over from *F*. The reaction tube, with potassium amide solution in *F*, the catalyst and glass tubing in the posterior end of *G*, is then disposed with leg *F* immersed in a bath of liquid ammonia and *E* connected with the stock cylinder of liquid ammonia, as shown in Figure 16 (*cf.* Fig. 8).

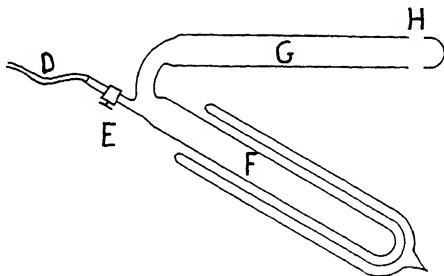


FIG. 16

Opening stopcock *E* just before the pressure in the reaction tube has fallen to that of the atmosphere, this to clear the tube *D* of air, and with a gentle current of ammonia escaping from *B* (Fig. 8) through *C*, the end of *G* is removed, along with the catalyst wire and the glass tube potassium container, by cutting a mark with a file at a point *H* near the end of the tube and touching the mark with a hot glass point. Simultaneously with opening *G*, stopcock *C* is set to establish a current of ammonia through *G* to the atmosphere, thus preventing the entrance of air into the reaction tube. Following the removal of the wire spiral and the bit of glass tubing a quantity of lead iodide equivalent to the potassium amide in leg *F* is introduced into leg *G* after which the tube is closed following the procedure already described.

After the seal has cooled, the ammonia bath is removed from *F*, the reaction tube is disposed in an upright position in an ice and water bath (*cf.* Fig. 12) and the desired amount of ammonia is distilled into *G*, following which the

<sup>8</sup> Franklin, *J. Am. Chem. Soc.*, 27, 843 (1905).

connection at *E* is severed. The operator now has in his hands a reaction tube containing potassium amide and lead iodide in its respective branches *F* and *G*. On pouring lead iodide solution into the solution of potassium amide a precipitate of lead imide is formed which is washed and removed from the reaction tube for analysis following a procedure which is now familiar.

**Preparation of Potassium Ammonoplumbite.**<sup>9</sup> Lead imide dissolves in excess of potassium amide to form a potassium ammonoplumbite. The following procedure yields this very soluble salt pure and beautifully crystallized.

Lead imide is precipitated and washed in the manner described above excepting that operations are begun by introducing the metallic potassium and catalyst into leg *F* of the reaction tube in order that the pure lead imide shall appear in *G*, the washings in *F* as shown in Figure 17. One then proceeds as follows to

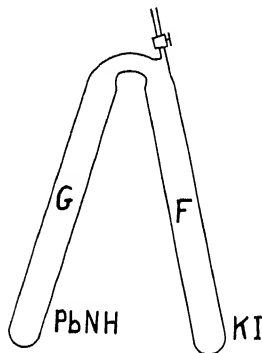


FIG. 17

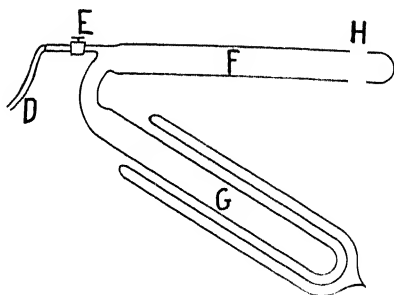


FIG. 18

remove the potassium iodide and catalyst and to prepare in leg *F* a solution of a quantity of potassium amide approximately equivalent to the lead imide contained in leg *G*. After distilling all the solvent from *F*<sup>10</sup> into *G*, taking care during this operation to collect and dry all the potassium iodide in the bottom of *F*, the reaction tube with leg *G* immersed in a liquid ammonia bath is connected with the ammonia supply tank as shown in Figure 18. Displacing the air in the connecting tube *D* after the manner already described, then with *E* and *C* wide open and *B* slightly open so that a slow current of ammonia is escaping at *C* (cf. Fig. 8), the posterior end of leg *F* is removed along with the iron wire catalyst, the potassium iodide formed by the interaction of potassium amide and lead iodide, and such other impurities as may be present. With a current of ammonia escaping through *F*, stopcock *C* having been set to arrest direct communication with the atmosphere, any material clinging to the interior walls of *F* is removed by means of a cotton swab moistened with liquid ammonia. A swab moistened with water, or even with dilute hydrochloric acid, may be used if necessary for efficient cleansing of the tube walls. After drying leg *F* a quantity of metallic potassium, approximately equivalent to the amount of lead imide contained in *G*, together with the catalyst, is introduced into leg *F* which is then closed in the manner already described. Stopcock *E* and valve *B* are then closed, the lead tube is unsealed at *H* and the liquid ammonia bath is removed from leg *G*. Hot *F* and cold *G* having taken on the temperature of the

<sup>9</sup> Franklin, *J. Phys. Chem.*, 15, 509 (1911).

<sup>10</sup> Note that *F* is always the leg of the reaction tube to which the stopcock is attached.

laboratory a portion of the liquid contained in *G* is poured into *F*. After the blue color of the potassium solution has completely disappeared and all the hydrogen generated has been removed the potassium amide solution contained in *F* is poured into *G*, whereupon the lead imide goes into solution. The solution of potassium ammonoplumbite thus formed, together with small quantities of insoluble material which are generally present, is transferred to *F* and allowed to stand until the suspended matter has settled after which the clear, colorless solution is decanted back into *G*.<sup>11</sup>

The walls of *F*, the arc of the reaction tube and the walls of *G* above the solution are rinsed by holding the reaction tube in such a position that ammonia condensed on the inner walls of *F*, of the stopcock tube and of *G* will run into the solution in *G*, and stroking the areas mentioned with a cotton swab saturated with liquid ammonia.<sup>12</sup> When *F*, the arc portion of *FG*, the stopcock tube and the walls of *G* above the solution are entirely free from salt, the reaction tube, with *G* in a bath of liquid ammonia and *E* connected with the cylinder *A* (Fig. 8), is set up as shown in Figure 19, care being taken to remove all

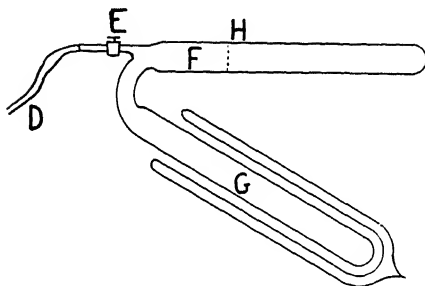


FIG. 19

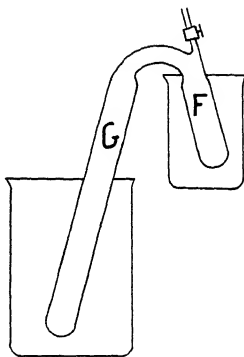


FIG. 20

the air from *D* which connects with cylinder *A* (Fig. 8). Leg *F* is then sealed off at the dotted line *H*, thus shortening this leg to what now constitutes, in effect, a small crystallizing vessel. Detaching the reaction tube at *E*, the purification of the salt is then conducted as follows. Ammonia gas is allowed to escape through *E* until the volume of the solution becomes such as to fill the leg *F* from one-half to two-thirds full. Pouring then the solution into *F*, the reaction tube is set up as shown in Figure 20 with the respective legs in separate baths of water. Dropping pieces of ice from time to time into the bath surrounding *G* this leg is maintained at a temperature lower than that of *F* under which conditions the solvent slowly evaporates from the solution in *F* and is condensed in leg *G*. By regulating the rate of evaporation a crop of beautiful crystals soon begins to grow. In case a salt crust begins to creep up the walls of the crystallizing vessel it can be dissolved and returned to the solution

<sup>11</sup> In the case of other compounds which are only moderately soluble, the process of purification by crystallization follows from here. Assuming, for example, we have in our hands a similar reaction tube containing potassium ammonoargentate made by dissolving silver amide in a solution of potassium amide, then a crop of crystals may be obtained simply by adjusting the solution to a proper concentration and cooling simultaneously the two legs of the reaction tube by immersion in liquid ammonia.

<sup>12</sup> Alternately, in case finely divided material might be carried back into *G* when following the above procedure, the rinsing is done with the tube in an upright position, the washings collecting in *F* being poured over into *G*.



by circumspectly mopping the walls of *F* above the solution with a cold cotton swab. The evaporation of the solution is continued until a satisfactory crop of crystals has been deposited. The mother liquor is then poured over into *G* following which operation the walls of the reaction tube are cleansed of adhering salt solution by the use of a cold mop as explained above. Distilling solvent from *G* into *F* the crop of crystals is brought into solution in fresh solvent whereupon the procedure described above is repeated and then, it may be, yet again. If for any reason the salt separates as a mush of minute crystals one does well to bring the salt back into solution and start the crystallization process anew.<sup>13</sup>

With the pure salt—partly in the form of solution—in *F*, mother liquor in *G*, and with the walls of the reaction tube rinsed free from solution—and not neglecting small amounts of solution or dry salt which may have gained entrance to the stopcock-tube—legs *F* and *G* are simultaneously cooled by immersion in liquid ammonia, following which connection is made with the supply of ammonia gas after the manner already described, thus giving the arrangement shown in Figure 21. Preparatory to sealing apart the legs *F* and *G*, stopcock *H* and the open ends of the Dewar tubes are protected by asbestos paper shields. Leg *G* is then detached from *F*, using for the purpose a small hand blast lamp. Leg *G* containing the mother liquor is set aside. (Figure 23.) Allowing time for the seal to cool stopcock *H* and valve *B* are closed, the container *F* is unsealed from the lead tube and, after removal of sealing wax from the stopcock exit, is attached, still immersed in its bath of liquid ammonia, to a Töpler pump as shown in Figure 22.

Setting the pump in action ammonia is removed from *F* until, with the disappearance of the solution, the pressure within the system shows a sharp decline,<sup>14</sup> at which juncture *F* is disconnected from the pump, allowed to warm up to laboratory temperature and weighed. Connecting *F* again with the pump it is evacuated at laboratory temperature and again weighed. Finally the tube is evacuated at 90°, cooled, and weighed, following which it is delivered of its contents, dried and weighed empty, following the procedure already described in detail for the removal of silver amide from its container, excepting that the products of the hydrolysis of potassium ammonoplumbite are dissolved in dilute acetic acid. Quantitative determinations of the amount of lead, potassium and ammonia contained in this solution together with the weighings described give the data necessary for calculating the composition of the compounds obtained.

From the mother liquor set aside in *G*, Figure 23, a second crop of crystals may be obtained following the procedure herewith described.

The tip of container *G* is opened and drawn out in the form of a long narrow delivery tube as shown in Figure 24, care being taken to avoid entrance of moisture or air to the tube during the operation. *G* (Fig. 24) is then set aside to be taken up later.

A reaction tube to which a tubulure *H* has been sealed, Figure 25, is connected with the small cylinder of ammonia (*A*, Fig. 8) in the now familiar manner. With a gentle current of ammonia passing the reaction tube, one proceeds with the operation of drying its three branches and closing the two legs *F'* and *G'* at the dotted marks. Maintaining a current of ammonia through the reaction tube, now out by way of tubulure *H*, placing a bath of liquid ammonia in position surrounding leg *G'*, Figure 26, the mother liquor is transferred from *G* to leg *G'*. The container *G*, Figure 24, is removed from its bath and warmed in the

<sup>13</sup> Instead of following the procedure just described the salt may be obtained well crystallized by evaporating the solution to proper concentration at laboratory temperature and then cooling slowly and carefully to the temperature of boiling ammonia.

<sup>14</sup> At  $-40^{\circ}$  the crystals show a slight vapor pressure in consequence of which, even at this low temperature, long-continued pumping removes ammonia of crystallization from the compound.

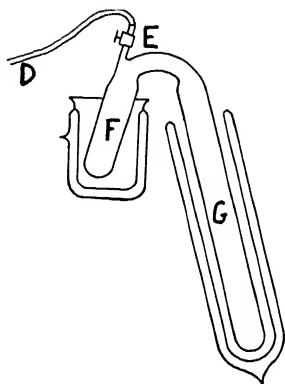


FIG. 21



FIG. 22



FIG. 23

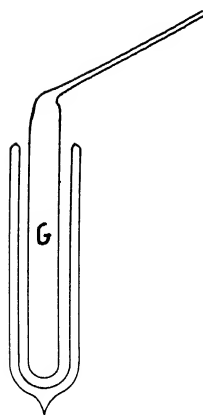


FIG. 24

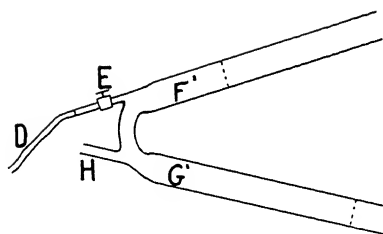


FIG. 25

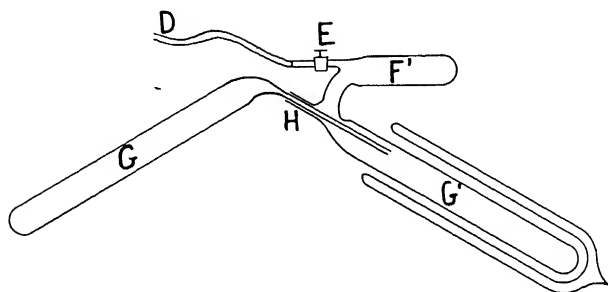


FIG. 26

region of the surface of the solution by contact with the operator's fingers until the pressure within is slightly above that of the atmosphere.<sup>15</sup> The slim delivery tube is then opened and inserted through tubulure *H* into the position shown in Figure 26. Rotating now container *G* on the axis of its stem the solution runs quietly into *G'*. Partly withdrawing *G*, it is held with its exit in the upper warmer portion of *G'* until any drops of solution clinging to the tip of the delivery tube shall have evaporated away. The stem of *G* may now be withdrawn from *G'* without danger of smearing the walls of *H* with salt solution which on drying leaves an explosive residue. Closing now *H* by means of a hand blast lamp, removing the liquid ammonia bath and disconnecting the reaction tube from the ammonia cylinder one proceeds to prepare a second crop of crystals following the steps already described.

Having described in detail these somewhat elaborate procedures it becomes unnecessary to concern ourselves further with this subject, other than to give the following references to papers in which a considerable variety of manipulation details are described.

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<sup>15</sup> The temperature of a bath of liquid ammonia open to the atmosphere is always well below the boiling point of the liquid whence it follows that the vapor pressure of the solution in *G* is below that of the atmosphere. Even when the temperature of the bath is slightly above its boiling point, as it is when the mouth of the Dewar vessel is closed with a plug of cotton wool, the temperature of *G* will drop when removed from the bath as the result of the evaporation of the film of liquid ammonia removed with *G* from the bath. The entrance of even a trace of atmospheric air brings about a blackening of the clear, colorless solution of potassium ammonio-plumbite.

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## AUTHOR INDEX

- Albrecht, 262  
 Angeli, 144, 211, 306  
 Askenasy and Grade, 132  
  
 Backer, 155, 157  
 Baly, Heilbronn and Hudson, 128  
 Bamberger, 157, 158, 289, 291, 293, 296,  
     300, 306, 307  
 Bamberger and Hauser, 304  
 Bamberger and Landsteiner, 158, 294  
 Bamberger and Lorenzen, 271  
 Bamberger and Rising, 307  
 Bamberger and Schuetz, 231  
 Bamberger and Seligmann, 236, 237  
 Bamberger and Stiegelmann, 307  
 Bamberger and Storch, 158, 295  
 Bamberger and Tschirner, 234  
 Bamberger and Vuk, 234  
 Bamberger and Wetter, 292  
 Bannow, 104  
 Bassett and Durant, 176  
 Bauer, 155  
 Beckmann and Fellrath, 271  
 Behrend, 169, 170  
 Beilstein and Gunther, 133  
 Beilstein and Wiegand, 169  
 Benedict, 266  
 Berg, 132, 158, 182, 183  
 Berglund, 168  
 Bergstrom, 27, 48, 58, 60, 61, 62, 63,  
     67, 68, 69, 70, 74, 77, 78, 139, 140,  
     191, 258  
 Bergstrom and Fernclius, 55, 292  
 Bergstrom, Gilkey and Lund, 222  
 Bergstrom and McAllister, 258  
 Besson, 161  
 Besson and Rosset, 160, 205  
 Billiter, 118  
 Biltz, 215  
 Bischoff, 253  
 Blacker, 117  
 Blair, 88, 112, 114, 115, 116, 118, 119,  
     125  
 Blair and Braham, 89, 97  
 Blix and Wirbelauer, 135, 137, 190  
 Bohart, 57, 59, 62, 69, 318  
 Bone and Perkin, 99  
  
 Bonnefoi, 224  
 Branch and Clayton, 273  
 Bray, 144, 206  
 v. Braun, 210, 271  
 Bray and Dowell, 179  
 Brønsted, 26  
 Browne and Hoel, 147  
 Browne, Holmes and King, 48  
 Browne and Houlehan, 27, 146  
 Browne and Wilcoxon, 141, 143  
 Bruce, 117  
 Burdick, 100, 107  
 Burgess and Ross, 50  
 Burgess and Smoker, 50  
 Busch, 243, 247  
 Busch and Leefhelm, 250  
  
 Cady, 19  
 Cady and Taft, 41, 48  
 Carvello, 88  
 Castner, 129  
 Chablay, 50, 51, 52, 225  
 Chamberlain, 189  
 Chapin, 177  
 Chapman and Thorp, 233  
 Chapman and Vodden, 191  
 Chattaway, 294  
 Chattaway and Wadmore, 195  
 Chuck, 143, 146, 150, 190, 229  
 Chauvenet, 140  
 Clark, 176  
 Clifford, 52  
 Claus, 117  
 Comey and Jackson, 64  
 Conrad and Bischoff, 297  
 Conroy, 133  
 Cooke, 147  
 Cornell, 193, 260, 264, 268  
 Cottrell, 20  
 Couldrige, 160, 161  
 Curtius, 144, 148, 277, 303, 304, 305  
 Curtius and Darapsky, 146, 214, 285  
 Curtius and Rissom, 146, 148  
  
 Dafert and Miklaus, 55  
 Dains and Brewster, 52  
 Dains, Greider and Kidwell, 118, 124

- Dar Juan, 235  
 Darzens, 193  
 Davis, 89, 97, 101  
 Davis and Abrams, 197  
 Davis and Blanchard, 119  
 Davis, Olmstead and Lundstrom, 27  
 Davy, 161  
 Degner and v. Pechmann, 155  
 Delépine, 241, 242  
 Dennstedt and Göhlich, 144  
 Deslandres, 55  
 Dickinson and Raymond, 241  
 Dimroth, 60, 294, 295, 299  
 Dimroth and Pfister, 288  
 Divers, 26, 28  
 Divers and Haga, 168, 169  
 Divers and Ogawa, 175  
 Drechsel, 95, 131, 132  
 Duden and Scharff, 241  
 Dunstan and Goulding, 233, 234, 235  
  
 Eberhardt and Welter, 253  
 Eibner, 253, 254, 255  
 Einhorn and Mauermayer, 239  
 Eiskampf, Marguerite, 314  
 Elbers, 297  
 Elliott, 17  
 Elsey, 222, 274  
 Emich, 94  
 Ephraim, 118  
 Ephraim and Gurewitsch, 170  
 Ephraim and Michel, 170  
 Ephraim and Piotrowski, 175  
 van Erp, 157  
 Eucken and Donrath, 16  
 Eucken and Karwat, 16  
 Euler and Euler, 283  
 Ewan and Young, 89  
  
 Fehrman, 261  
 Fernelius, 138, 198, 299  
 Fichter and Brunner, 58  
 Fischer, 247, 264, 293, 296, 304, 306,  
 308, 309  
 Fischer and Schröter, 59  
 Fitzgerald, 56, 59, 60, 64, 78, 139, 222  
 Forster, 295  
 Foerster and Gunther, 64  
 Fowler, 62  
 Franchimont, 157, 170  
 Franchimont and Klobbie, 155, 157  
 Franchimont and Umbgrove, 156, 158  
 François, 80  
 Frankenburger, Andrusso and Dün, 70  
 Frankland, 59  
 Franklin, 17, 26, 27, 34, 50, 54, 55, 57,  
 61, 68, 71, 72, 75, 76, 78, 80, 83, 85,  
 90, 92, 94, 99, 102, 104, 105, 129,  
 130, 131, 133, 142, 146, 148, 169, 188,  
 228, 273, 280, 311, 319, 323, 325, 326  
 Franklin and Cady, 19  
 Franklin and Gibbs, 224  
 Franklin and Hine, 135, 138  
 Franklin and Kraus, 16, 17, 20, 24, 27,  
 77, 88, 95, 113, 155, 156, 273, 311  
 Franklin and Stafford, 95, 169, 274, 311  
 Friedrichs, 211  
 Fulton, Ruth V., 95, 110, 274, 275, 277  
 Fulton and Bergstrom, 48  
 Furth, 80  
  
 Gal, 59, 115, 275  
 Gambier and Brochet, 253  
 Garrett, 78  
 Gattermann, 179  
 Gattermann and Schnitzspahn, 208  
 Gautier, 134  
 Gay Lussac and Thénard, 53  
 Gerhardt, 161  
 Gibbs, 222  
 Gilpin, 163  
 Goldschmidt, 148, 178, 297  
 Goodyear, 146  
 Gore, 19  
 Götzky, 145  
 Goudechon, 80  
 Goudrian, 64  
 Granichtstädten and Werner, 260  
 van de Griendt, 248  
 Griess, 295  
 Griffith, 92  
 Griswold, 17, 92, 97, 299  
 Guntz, 55  
 Gutmann, 195, 216  
  
 Haag, 99  
 De Haas, 233  
 Haber, 216  
 Haller and Bauer, 245  
 Hallmann, 210  
 Hantzsch, 64, 67, 127, 154, 156, 196,  
 291, 297, 309  
 Hantzsch, Bauer and Hofmann, 127  
 Hantzsch and Holl, 170  
 Hantzsch and v. Hombostel, 262  
 Hantzsch and Kaufmann, 309  
 Hantzsch and Kissel, 298  
 Hantzsch and Kraft, 260  
 Hantzsch and Mai, 204  
 Hantzsch and Osswald, 97

- Hantzsch and Reddelien, 291  
 Hantzsch and Stuer, 169, 170  
 Hantzsch and Wachter, 293  
 Harker, 146  
 Hart, 99, 149, 194  
 Hartung, 201  
 Hashimoto, 189  
 Henderson and Gallety, 59, 62  
 Hendricks and Pauling, 146  
 Henke, 157  
 Henle, 225  
 Hinsberg, 314  
 Hinsberg and Koller, 252  
 Hirzel, 60  
 Hoff, 158  
 Hofmann, 89, 97, 120, 160, 206  
 Hofmann, Hartmann and Nagel, 28, 83  
 Hofmann, Hartmann and Kroll, 216  
 Hofmann and Hock, 309  
 Hofmann and Kroll, 212, 216  
 Hofmann and Marburg, 80  
 Holmes, 83  
 Holzwardt, 285  
 Hübner, 234  
 Hugot, 165  
 Hunter and Partington, 154  
  
 Jackson and Menke, 166  
 Jacobsohn, 166, 171  
 Jakowin, 178, 200  
 Jameson, Adelaide, 184  
 Japp and Moir, 251  
 Joannis, 20, 143, 165, 201  
 Johnson, Morey and Kott, 138  
 Johnson and Sidwell, 138  
 Joly, 98  
  
 Kaess and Gruskiewicz, 202  
 Kahlenberg and Ruhoff, 224  
 Kane, 81  
 King, 188  
 Kirk and Browne, 41  
 Kirkish, 268  
 Kirpal, 157  
 Kjellin, 216  
 Knoevenagel, 249  
 Knudsen, 239  
 Koepfli, 189  
 Krall, 91, 101  
 Kraus, 20, 50, 67  
 Kraus and Cuy, 54, 55  
 Kraus and Hurd, 59  
 Kraus and Kawamura, 51  
 Kraus and Rosen, 51  
  
 Kraus and Whyte, 49, 55  
 Kudernatsch, 242, 313  
  
 Lachman, 289  
 Lachowicz, 247, 248, 257  
 Lander, 280  
 Lange, 283  
 Langmuir, 45, 191  
 Laurent and Gerhardt, 107  
 Lebeau, 50, 225  
 Le Blanc and Bergmann, 65  
 Le Blanc and Weyl, 65  
 Lemoult, 164  
 Lengfeld, 135, 136  
 Lengfeld and Stieglitz, 176, 204  
 Leuckhardt, 117  
 Lewis, 40, 164  
 Ley, 209  
 Ley and Shafer, 113  
 Liebig, 87, 102, 107  
 Liebig and Wöhler, 118, 160, 161  
 Lieke, 247  
 Limpricht, 233  
 Lindemann and Thiele, 145  
 Linnemann, 197  
 Löb, 201  
 Lobry de Bruyn, 211  
 Lossen and Schifferdecker, 284  
  
 Maas and Hatcher, 211  
 Madelung and Kern, 87, 100, 101, 104,  
     106, 119, 122, 123  
 Maquenne, 133  
 Marekwald, 314  
 Marekwald and Wille, 177, 179, 181  
 Mathews, 186, 314  
 Meisenheimer, 235  
 Meldola and Streetfield, 299  
 Mendelejeff, 197  
 v. Meyer, 215, 285, 298  
 Meyer and Hopff, 129  
 Meyer and Lecco, 296  
 v. Meyer and Müller, 297  
 Michael and Hibbert, 283  
 Michael and Wing, 208  
 Michaelis, 164, 165, 176, 206  
 Michaelis and Herz, 176  
 Michaelis and Luxembourg, 206  
 Michaelis and Schindler, 176  
 Michaelis and Storbeck, 176  
 Michaelis and Schroeter, 166, 206  
 Michaelis and Silberstein, 163  
 Michaelis and Soden, 164  
 Mignonac, 260  
 Miller and Kendrick, 84

- v. Miller and Plöchl, 253, 254  
 v. Miller, Plöchl and Rohde, 262  
 Moureu and Mignonac, 260, 262  
 Moore, 260  
 Mulder, 313  
  
 Nägeli, 262  
 Nef, 283  
 Niemann, 91, 116, 208, 271, 279  
 Nietzki and Benckiser, 215  
 Noyes, 44, 178, 179, 191  
  
 Ogg and Bergstrom, 258  
 Ott, 193, 262  
 Ott and Ohse, 195  
 Otto, 248  
  
 Pauling, 42, 139, 145, 191  
 Pauly, 262  
 Pauly and Waltzinger, 189  
 v. Pechmann, 209  
 v. Pechmann and Frobenius, 296, 299  
 v. Pechmann and Manck, 284  
 Pellizzari, 285  
 Pellizzari and Cantoni, 203  
 Pellizzari and Tivoli, 203  
 Perpérot, 165  
 Pesci, 60, 80  
 Piccini, 216  
 Pinck and Blair, 118, 125  
 Pinner, 186, 263, 265, 268, 280  
 Pinner and Klein, 268  
 Plantamour, 60  
 Plöchl, 247  
 Porter, 43  
  
 Rakshit, 275  
 Raschig, 57, 167, 168, 177, 179, 181,  
     196, 244  
 Rathke, 102  
 Rây, 80  
 Rengade, 49, 226  
 Reynolds, 136  
 Richardson, 206  
 Rideal, 191  
 Riehm, 262  
 Robin, 247  
 Romburgh, 313  
 Rose, 161  
 Rosenheim, 61  
 Rosenheim and Braun, 77  
 Ruff, 34, 137  
 Ruff and Albert, 190  
 Ruff and Eisner, 137  
  
 Ruff and Geisel, 55, 172, 174  
 Ruff and Georges, 55  
 Ruff and Treidel, 138  
 Ruspagiari, 115  
  
 Scheibler, 128  
 Scheidemann, 276  
 Schenck and Römer, 205, 206  
 Schlenk, 58  
 Schmidt, 150  
 Schneider, 188, 197  
 Schrader, 49, 54  
 Schroeter, 209  
 Schumann, 175, 176  
 Schurman and Fernelius, 47, 48  
 Schwarz and Denk, 190  
 Schwarz and Giese, 288  
 Schwarz and Schenk, 138  
 Schwarz and Sexauer, 137  
 Seely, 19  
 Selewanew, 191  
 Sell and Zierold, 203  
 Sherry, 19  
 Shinn, 224  
 Short, 122, 181  
 Sidgwick, 43, 45, 82  
 Sidgwick, Sutton and Thomas, 153  
 Siepermann, 110  
 Sloan, 17, 57  
 Smith, F. A., 17  
 Smith, G. E. P., 120, 123, 127, 260  
 Snape, 120  
 Sommer, 301  
 Sommer and Pincas, 144, 301  
 Spencer, 196  
 Stähler, 89, 133, 137, 201  
 Stähler and Denk, 78, 138  
 Stieglitz, 290  
 Stieglitz and Brown, 214  
 Stieglitz and Leech, 216  
 Stieglitz and Senior, 211  
 Stock, 179  
 Stock and Blix, 188  
 Stock and Holle, 188  
 Stock and Pohlund, 16  
 Stock and Zeidler, 135, 137  
 Stokes, 163, 164, 205  
 Stollé, 202, 304  
 Stollé and Hofmann, 203  
 Strain, 17, 130, 240, 241, 243, 248, 250,  
     255, 259  
 Strain and Smith, 16  
 Strecker, 273  
 Strömholm, 80  
 Sudborough and Hibbert, 228

- Tafel and Wassmuth, 277  
Tanatar, 145, 216  
Taylor and Rinkenbach, 195  
Thiele, 142  
Thiele and Lachman, 154, 156  
Thomae, 259  
Thomas and Pugh, 138  
Thomas and Southwood, 138  
Thorpe and Tutton, 166  
Titherley, 55, 56, 190, 226  
Traube, 169, 170, 202, 259  
Traube and Brehmer, 167, 169  
Traube and Reubke, 169, 170  
Tscherniak, 182  
Turrentine, 48, 141, 148  
Turrentine and Moore, 48, 146  
  
Usherwood, 129  
  
Vidal, 161, 162  
Vigorous and Hugot, 135  
Vogel and Partington, 176  
Volhardt, 107  
  
Wagner, 211  
Wallach, 208  
Wallach and Hoffmann, 209  
Wanklyn and Chapman, 233  
  
Weiser, 56  
Weiss and Engelhardt, 190  
Weith, 201, 202, 207  
Weitz, 77  
Welsh and Broderson, 211  
Wenzel, 190  
Werner, A., 65, 139  
Werner, E. A., 114, 127  
Werner and Bell, 99  
Weyh, 19  
Wheeler and Jamieson, 99  
White, 51  
White and Kirschbaum, 62  
White and Knight, 49, 52  
Wieland, 203, 290, 308, 309  
Wieland and Maier, 213  
Willstätter and Wirth, 283  
Wippermann, 283  
Wislicenus, W., 143  
Wohl, 304, 306  
Wohl and Schiff, 310  
Wood, D., 128  
Wood, J. K., 64  
Wooster, 42  
Würtz, 182  
  
Zimmermann, 102  
Zorn, 309





## SUBJECT INDEX

- Acid amide-chlorides, 200
- Acid amidines, 263
- Acetic anammonide, 191
- Acid amides, 272
- Acid anammonides, 36, 188
- Acid anammonides, mixed, 192
- Acid anhydride-anammonides, 197
- Acid chlorides, 200
- Acid imide-chlorides, 200
- Alcohols, ammono, 217, 219
- Aldehyde-alcohols, 238
- Aldehyde-ethers, 238, 258
- Aldehyde-esters, 238
- Aldol condensation, 249, 257
- Alkylamines, 222
- Alkylisocyanides, 133
- Allophanic acid, 117
- Alphylguanidines, 92, 118
- Aluminum nitride, 60
- Amidosulfuric acid, 167
- Ammonates, 38
- Ammonation, 39
- Ammonia of crystallization, 38
- Ammonium salts, as acids, 26
- Ammono acids, 35
- Ammono alcohols, 37
  - cyclic, 237
  - primary, 221, 230, 232
  - secondary, 221, 235
  - tertiary, 222, 236
- Ammono bases, 35, 51
- Ammonobasic salts, 36, 75
- Ammono ethers, 37, 235
- Ammonolysis, 39
- Ammonous nitrides, 56, 60, 62
- Amphoteric amides and imides,
  - alkali metal salts of, 64
- Aquo acids, 35
- Aquo-ammono acids, 35
- Aquo-ammono salts, 35
- Aquo bases, 35
- Aquobasic ammonobasic salts, 84
- Aquo salts, 35
- Augmentation and reduction, 39, 47
  
- Barium amide, 58
- Barium nitride, 58
  
- Basic nitrides, 51
- Benzenesulfonyl nitramide, 314
- Benzoic acid amide-chloride, 208
- Benzoine condensation, 244, 250, 257
- Benzylideneimine, 243
- Benzylidenephénylimine, 255
- Beryllium nitride, 58
- Biguanide, 86
- Biuret, 117, 118
- Bismuth nitride, 61
- Boric anammonide, 188
- Bromine azide, 196
  
- Cadmium amide, 59
- Cadmium nitride, 59
- Calcium amide, 58
- Calcium nitride, 58
- Cannizzaro reaction, 244, 251, 257
- Carbamic acid, 108, 111
- Carbazylic acid salts, 266, 273
  - pyrogenetic decomposition, 268
- Carbazylic acids, 38, 263
  - salts of, 266
- Carbazylic acids, cyclic, 277
- Carbonic acids, ammono, 86
- Carbonic acids, aquo-ammono, 108
- Carbonic acids, cyclic, 101, 121, 124
- Carbonic anammonide, 188
- Carbonic nitride, 86
- Carbon monoxide, 132
- Carbonous acid, ammono, 128
- Carbon tetrachloride, 201
- Carbonylcarbamic acid, 117, 119
- Carbonylguanidine, 117, 121
- Carbonylurea, 117, 119
- Carboxazylic acid salts, pyrogenetic decomposition, 277
- Carboxazylic acids, 38, 272
  - salts of, 274
- Carboxazylic acids, cyclic, 276
- Carbylic acid amide-chlorides, 208
- Carbylic acid chlorides, 206
- Carbylic acid imide-chlorides, 208
- Chloramine, 177
- Chlorineazide, 196
- Chlorine trinitride, 191
- Chloroform, 206

- Cobaltous nitride, 62  
Cuprous nitride, 56  
Cyanamide, 86, 93  
Cyan carbamic acid, 117, 120  
Cyanic acid, 108  
Cyanmethine, 285  
Cyanogen, 192  
Cyanogen chloride, 195, 202  
Cyanurea, 117, 121  
Cyanuric trichloride, 204  
Cyanurtriazide, 194  
Cyanurtricyanide, 193  
Cyclic carbylic acids, 267, 276
- Deammonation, 39  
Deelectronation, 41  
Diazoaminobenzene, 299  
Diazobenzene, 291  
    and hippurylhydrazine, 305  
    and hydrazine, 303  
    and hydroxylamine, 305  
    and phenylhydrazine, 304  
    and phenylhydroxylamine, 306  
Diazobenzeneamide, 294  
Diazo compounds, 288, 290  
Dicarbonic acids, 98, 117  
Dichloramine, 177  
Dicyandiamide, 86, 98  
Dicyandiamidine, 119  
Dicyanamide, 86, 100  
Dimethylnitramide, 156, 158
- Electronation, 41  
Ethylchloramine, 182  
Ethylchloramine, 182  
Ethylideneimine, 241  
Ethylidenephnylimine, 254
- Formic acid imide-chloride, 208  
Formic anammonide, 191
- Germanic acids, ammono, 138  
Germanic nitride, 190  
Gold amide-imide, 57  
Grignard reactions, 227, 250, 256  
Guanidine, 86, 88  
Guanylcabamic acid, 117, 118  
Guanylurea, 117, 119
- Hexachlorethane, 207  
Hexamethylenetetramine, 239  
Hydrazine, 211, 213  
Hydrazoic acid, 141  
Hydrobenzamide, 246  
Hydrocyanic acid, 128, 130
- Hydrogen peroxide, 211, 212  
Hydromelonic acid, 86, 106  
Hydroxylamine, 211, 215  
Hypochlorous acids, ammono, 177  
Hypochlorous anammonide, 191
- Imidodicarboxylic acid, 117, 118  
Imidodisulfamide, 170  
Imidosulfuric acid, 169  
Iodine azide, 196  
Isoamylnitramide, 158
- Ketone-alcohols, 259  
Ketone-ethers, 259
- Lead imide, 61, 325
- Liquid ammonia,  
    as solvent, 19  
    augmentation and reduction in, 39  
    properties, 15  
    manipulations, 317  
    metathetic reactions in, 25  
    nitridation in, 47  
    oxidation in, 47
- Liquid ammonia solutions,  
    conductance of, 17  
    optical activity, 19  
    velocities of ions in, 18
- Lithium amide, 55  
Lithium ammonoaluminate, 68  
    ammonoferrate, 70  
Lithium imide, 55  
Lithium nitride, 55
- Magnesium amide, 58  
Magnesium nitride, 58  
Manganese amide, 61  
Melamine, 86, 101  
Melon, 86  
Mercuric nitride, 59  
Mercuric salts, ammonated, 82  
Mercuric salts, ammonobasic, 83  
Mercuric salts, mixed aquobasic am-  
    monobasic, 84  
Mercury nitrogen compounds, 80  
Methylnitramide, 155  
Mixed acids, 185
- Nickel amide, 62  
Nickel nitride, 62  
Nitric acid, ammono, 141  
    aquo-ammono, 154  
Nitramide, 154  
Nitridation, 39  
Nitridizing agents, 47

Nitrido sulfuric acid, 169  
 Nitriles, 282, 284  
 Nitrogen chains, 307  
 Nitrogen system, 30  
 Nitrosamines, 238  
 Nitrous acid, aquo-ammono, 300  
 Nitrous acid and hippurylhydrazine, 304  
     and hydrazine, 301  
     and phenylhydrazine, 304  
     and phenylhydroxylamine, 305  
     and hydroxylamine, 305  
 Nitrous oxide, 143, 197  
 Nomenclature, 35  
  
 Phenylisocyanide dichloride, 203  
 Phenylnitramide, 158  
 Phospham, 161  
 Phosphoric acids, ammono, 160  
     aquo-ammono, 163  
 Phosphoric nitride, 190  
 Phosphorous acids, ammono, 164  
     aquo-ammono, 166  
 Phosphorous nitride, 190  
 Plus and minus signs, 43  
 Polycarbonic acids, 101, 124  
 Potassium amide, 51  
 Potassium ammonoaluminate, 67  
     ammonoargentate, 71  
     ammonobariate, 72  
     ammonoberylliate, 68  
     ammonocadmiate, 69  
     ammonoceriate, 74  
     ammonocalciate, 72  
     ammonocuprite, 70  
     ammonogalliate, 74  
     ammonohypomanganite, 69  
     ammonolanthanate, 74  
     ammonolithiate, 73  
     ammonomagnesiate, 68  
     ammononickelate, 70  
     ammonoplumbite, 66, 326  
     ammonosodiate, 72  
     ammonostannate, 139  
     ammonostannite, 139  
     ammonostrontiate, 72  
     ammonothallite, 71  
     ammonotitanate, 137

Potassium (Cont.)  
     ammonozincate, 65  
 Pyridine, 258  
  
 Rubidium amide, 56  
 Rubidium ammonolithiate, 74  
     ammonosodiate, 73, 74  
  
 Schiff's bases, 252  
 Silicic acids, ammono, 135  
 Silicic anammonide, 190  
 Silver amide, 57, 319  
 Sodium amide, 54  
 Sodium ammonoaluminate, 68  
     ammonoberylliate, 68  
     ammonohypomanganite, 70  
     ammonomagnesiate, 69  
     ammonostannite, 140  
 Stannous imide, 140  
 Strontium amide, 58  
 Strontium nitride, 58  
 Sulfamide, 169  
 Sulfazylic acid, 176  
 Sulfimide, trimolecular, 171  
 Sulfonic acids, aquo-ammono, 311  
 Sulfuric acids, aquo-ammono, 167  
 Sulfurous acids, ammono, 172  
 Sulfurous acids, aquo-ammono, 175  
  
 Tetrasulfurtetranitride, 173, 174  
 Thallous nitride, 61  
 Thorium amide, 140  
 Thorium imide, 140  
 Thorium nitride, 190  
 Titanic acids, ammono, 137  
 Trichlorbutane, 207  
 Trichlorethane, 207  
 Trichloropropane, 207  
 Tricyanmelamine, 86, 104  
 Tungsten nitride, 190  
  
 Unicarbonic acids, 88, 108  
 Urea, 86, 114  
  
 Zinc amide, 59  
 Zinc nitride, 59  
 Zirconic acids, ammono, 138  
 Zirconium nitrides, 190



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